

CORROSION MECHANISMS FOR CEMENTED SOILS IN THREE DIFFERENT SULFATE SOLUTIONS

Pengju Han

Taiyuan University of Technology,
College of Architecture and Civil Engineering
Taiyuan, Shanxi 030024 P. R. China

Chao Ren

Taiyuan University of Technology,
College of Architecture and Civil Engineering
Taiyuan, Shanxi 030024 P. R. China

Xiaohong Bai

Taiyuan University of Technology,
College of Architecture and Civil Engineering
Taiyuan, Shanxi 030024 P. R. China

Y. Frank Chen (corresponding author)

The Pennsylvania State University,
Department of Civil Engineering
Middleton, PA 17057, USA
E-mail: yxc2@psu.edu

Keywords

cemented soil, compressive strength, corrosion mechanism, sulfate, pollution, solution

Abstract

In order to simulate and study the corrosion effects on the compressive strength of cemented soils that could be exposed in a polluted environment, a series of tests were conducted on cemented soil blocks cured with different concentrations of H_2SO_4 , $MgSO_4$, and Na_2SO_4 solutions. The test results show that the corrosion degree generally increases with the corrosion time and the solution concentration, while the compressive strength decreases with the increasing corrosion degree. The corrosion degree is highest for the Na_2SO_4 solution, followed by the $MgSO_4$ and H_2SO_4 solutions. Namely, when the SO_4^{2-} ion exists in a solution, the corrosion degree for the positive ions follows this descending order: Na^+ , Mg^{2+} , and H^+ . X-ray diffraction (XRD) phase analyses were performed for the cemented soil samples after corrosion and ionic concentrations. The results show that the compressive strength decreases with an increase of the Mg^{2+} concentration in the $MgSO_4$ solution and the Na^+ concentration in the Na_2SO_4 solution. At the same time, the strength increases with an increase of the pH value of the H_2SO_4 solution. Based on the chemical analysis results, the corrosion of H_2SO_4 or $MgSO_4$ solutions on cemented soils is deemed as a composite action involving the combined resolving and crystallizing corrosion processes. Furthermore, the corrosion of the Na_2SO_4 solution of cemented soil is a composite action consisting of dissolving and crystallizing.

1 INTRODUCTION

The cemented soil technique is a method of mixing the cement with in-situ soils in order to improve the soil's properties. Cement-stabilized soils may or may not work in corrosive conditions. Cemented soils would be influenced under the environment of acid rain, seawater invasion, or industrial pollution. These adverse effects could result in a structural deterioration. At a corrosive site, the strength of the soil stabilized by the cement is increased at the beginning of the stabilization, but it will be decreased due to the deterioration over time. Cemented soils are utilized in a SO_4^{2-} corrosive environment when the groundwater is polluted or used under the seawater. Such a corrosive environment will inevitably corrode the cemented soil and thus change its mechanical properties. This serious issue must be considered in any practical project.

Several researchers have looked at the influence of a corrosive environment on the properties of cemented soils for various aspects. Venkatarama and Jagadish [1] performed an experimental study on the influence of soil composition on the strength and durability characteristics of soil-cement blocks. Walker [2] summarized

the results from a comprehensive investigation undertaken to assess the influence of soil characteristics and cement content on the physical properties of stabilized soil blocks. Pei and Yang [3] stated that the influence of Na_2SO_4 on cemented soils contributed to the diffusion of Na^+ and SO_4^{2-} and that their chemical reaction with $\text{Ca}(\text{OH})_2$ weakened the strength of the cemented soils due to decomposition and breaking. Shihata and Baghdadli [4] investigated the durability characteristics and compressive strength of cemented soils after a prolonged exposure to saline ground water. Jiao and Liu [5] analyzed the influence of the cement-soil strength in an acid environment. Koliass et al. [6] studied the effectiveness of high-calcium fly ash and cement in stabilizing fine-grained clayey soils in the laboratory. Ning et al. [7, 8] investigated the behaviors of cemented soils under various environmental conditions and concluded that, in contrast to the mechanical strength, the environmental corrosion had little effect on the fracturing process. Dong et al. [9, 10] tested the mechanical properties and electrical resistance of cement-soil polluted by H_2SO_4 . Iyengar and Al-Tabbaa [11] presented two effective magnesia-based cements for the stabilization/solidification (S/S) of contaminated soils. Xing et al. [12, 13] showed that Mg^{2+} , Cl^- , and SO_4^{2-} caused not only a change in the microstructures of salt-rich soil-cements, but also reduced the strength of the soil-cement composite. Zandieh and Yasrobi [14] proved that two polymer materials could be used to stabilize the polluted soils on road shoulders, slopes, and military and airport pads. Heineck et al. [15] analyzed the microstructural behavior of composite mixtures of residual soils and sodic bentonites that were used as contaminant barriers. They carried out a series of microstructural analyses, including X-ray diffraction (XRD), scanning electronic microscopy (SEM), and energy-dispersive spectrometry (EDS). Voglar and Lestan [16] set up a strength model that the formulations of ordinary Portland cement (OPC), calcium aluminate cement (CAC) and pozzolanic cement (PC) and additives were used for the solidification/stabilization (S/S) of soils from a contaminated industrial brownfield. Liu et al. [17] deduced the relationship between the ion concentration and the corrosion time based on the theory of chemical dynamics, damage mechanics, and the chemical reaction formula between MgCl_2 and the cement soil. Yang et al. [18, 19] considered the factors of cement content, curing age concentrations of magnesium sulfate, and pH value and concluded that the strength of the cemented soil increased with the cement content and curing age. They also analyzed the microscopic mechanism of failure. Nevertheless, studies on the influence of different sulfate solutions on the properties of cemented soils are still rather limited. To further investigate the corrosion effect

and process in a sulfate corrosion environment, a series of tests, including unconfined compressive tests, were conducted on the cemented soil blocks that were cured by H_2SO_4 , MgSO_4 , and Na_2SO_4 solutions with different concentrations. Photos of the blocks' appearances, XRD phase of the corrosion power of the cemented soils, and the concentrations of SO_4^{2-} , Mg^{2+} , H^+ or Na^+ in the corrosive solutions after curing the blocks were also measured. Corrosion mechanisms for different sulfate solutions on cemented soils were investigated.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

The main chemical composition of the cemented soils for testing is listed in Table 1. A summary of the materials and the mixing machine is provided as follows.

- (1) Soil: Air-dried silt soil with plasticity index (I_p) = 8.1, uniformity coefficient (C_u) = 26.67, and curative coefficient (C_c) = 1.35.
- (2) Cement: Ordinary Portland cement (OPC) with compressive strength = 32.5MPa after 28 days of curing, produced by a local cement company in Taiyuan, a northern city in China.
- (3) Proportion of cemented soil contents: soil in mass: cement: water = 100:20:50. Tap water is used for the cemented soil, and water content value in cemented soil = 29.4%. The cement content value is 11.8%.
- (4) Mixing machine: HJW-30 blender having a body volume = 30L and a rotational speed = 48 rpm.
- (5) Typical size of scaled cemented soil samples: $70.7 \times 70.7 \times 70.7 \text{ mm}^3$.
- (6) Standard curing time for the cemented soil prior to submersion with a sulfate solution: 7 days.

Table 1. Main chemical composition of cemented soils.

pH (-)	Ca^{2+} (mg/kg)	Mg^{2+} (mg/kg)	SO_4^{2-} (mg/kg)	Cl^- (mg/kg)	CO_3^{2-} (mg/kg)	OH^- (mg/kg)
9.80	427.84	354.17	2879.10	282.32	1090.8	496.64

2.2 Preparations of H_2SO_4 , MgSO_4 , and Na_2SO_4 solutions

Based on the Chinese national standards GB 50021 (2009) [20] and GB 50046 (2008) [21], the following concentrations of H_2SO_4 , MgSO_4 , and Na_2SO_4 sulfate solutions were considered in this study: 1.5g/L, 4.5g/L, 9.0g/L, and 18.0g/L. The corrosion results for the three solutions are summarized in Tables 2–4, in which the corrosion ratings were based on GB 50021 (2009) [20].

According to GB 50021 (2009) [20], the circumstance would be graded as B for samples fully cured by pure water. For either solution with lower concentration, the corrosion rating is consistent as weak (for 1.5g/L concentration) or medium (for 4.5g/L concentration), Tables 2–4. For higher concentration (9.0 or 18.0g/L), no consistency for the corrosion rating is noted.

Table 2. Chemical ingredients of H₂SO₄ solution and corrosion-evaluation results.

Concentration (g/L)	pH		SO ₄ ²⁻	
	Corrosion degree (g/L)	Corrosion rating	Corrosion degree (g/L)	Corrosion rating
1.5	5.4	weak	1.302	weak
4.5	4.3	medium	2.401	medium
9.0	2.0	strong	3.358	strong
18.0	1.6	strong	3.889	strong

Table 3. Chemical ingredients of MgSO₄ solution and corrosion-evaluation results.

Concentration (g/L)	Mg ²⁺		SO ₄ ²⁻	
	Corrosion degree (g/L)	Corrosion rating	Corrosion degree (g/L)	Corrosion rating
1.5	2.196	weak	0.960	weak
4.5	2.293	weak	2.000	medium
9.0	2.368	weak	2.168	medium
18.0	2.538	weak	2.500	medium

Table 4. Chemical ingredients of Na₂SO₄ solution and corrosion-evaluation results.

Concentration (g/L)	Na ⁺		SO ₄ ²⁻	
	Corrosion degree (g/L)	Corrosion rating	Corrosion degree (g/L)	Corrosion rating
1.5	0.521	no	1.001	weak
4.5	1.198	no	2.300	medium
9.0	1.461	no	2.805	medium
18.0	1.670	no	3.207	strong

2.3 Testing Procedure

The testing procedure consisted of the following steps.

- (1) Prepare the cemented soil blocks, as described in the above.
- (2) Cure the blocks with MgSO₄, H₂SO₄, and Na₂SO₄ solutions in five different concentrations, i.e., 0, 1.5, 4.5, 9.0 and 18.0g/L.

- (3) Photograph each soil block at the curing times of 3, 7, 14, and 28 days to observe the change in appearance during the corrosion process.
- (4) Conduct the unconfined compression tests for the blocks at the same curing time as described in Step 3. For each curing time, three blocks were tested simultaneously for each prescribed concentration in a solution. The average value from the three tests is used as the block strength.
- (5) Measure the main ionic concentrations of the solutions immediately after the blocks are removed.
- (6) Perform phase analyses for the cemented soil samples in powder form after corrosion using the TD 3500 X-ray diffraction (XRD) machine, made in Denmark. The cemented soil powder samples were taken from MgSO₄, H₂SO₄, and Na₂SO₄ solutions with a concentration of 18.0g/L. The XRD test was a continuous scan with a scanning angle of 200–700 and a scanning speed of 0.020/s. After the test, the corrosive powders were analyzed using JADE5.0 software to determine their chemical components [22].

3 RESULTS AND DISCUSSION

3.1 Change of block appearance

Figures 1–3 show the photographed appearances of the samples after 28 days of curing in the solutions. From these photos, it is clear that the sulfate solution changes the look of a cement-soil block by ways of peeling, size reduction, and cracking. Detailed observations are described as follows.

- (1) As shown in Figure 1, for the samples cured in the H₂SO₄ solution the main phenomena are peeling, size reduction, and increasing corrosion degree with the greater concentration.
- (2) Referring to Figure 2, for the MgSO₄ solution with a lower concentration (i.e., 1.5–4.5 g/L), only crystal-like material was seen on the surface. The change in the surface size is not obvious. However, for a higher concentration (i.e., 9.0–18.0g/L), the corrosion degree becomes more serious so that both crystal-like material and peeling were observed. The corrosion degree is less than that in the H₂SO₄ solution. At the onset of the surface peeling, the soil sample started to crack at a concentration of 18.0g/L.
- (3) For samples in the more dilute Na₂SO₄ solution with the lower concentration (1.5–4.5g/L), similar to the MgSO₄ solution only crystal-like material was observed on the surface (Figure 3). For a higher concentration (9.0–18.0g/L), the corrosion degree is more significant and the sample begins to break. For samples cured in the solution with the concentration of 18.0g/L, the damage was too severe to perform a strength test.

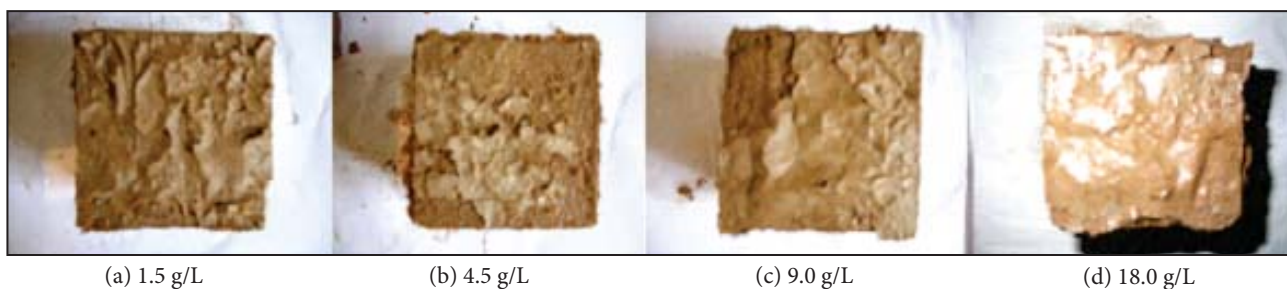


Figure 1. Photos for the sample blocks in the H₂SO₄ solution after 28 days of curing.

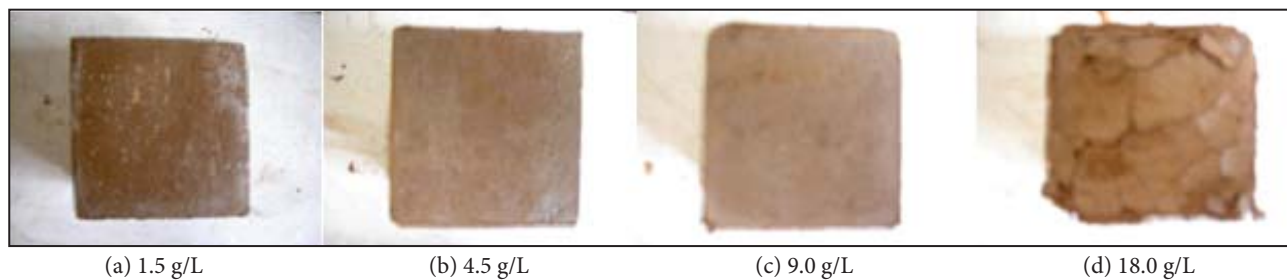


Figure 2. Photos for the sample blocks in the MgSO₄ solution after 28 days of curing.

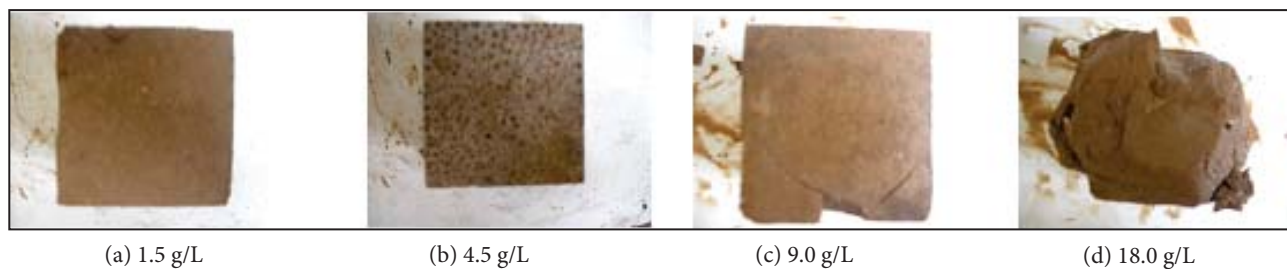


Figure 3. Photos for the sample blocks in the Na₂SO₄ solution after 28 days of curing.

Based on the above observations, the influence of the sulfate solution on the soil blocks increases with the increase of the solution concentration and the curing time. For inorganic compounds with a high solution concentration (9.0-18.0g/L), the influence degree for the three solutions follows such a descending order: Na₂SO₄ > MgSO₄ > H₂SO₄. Namely, when the SO₄²⁻ ion exists in a solution, the positive Na⁺ ion has the highest corrosion degree, followed by Mg²⁺ and H⁺.

3.2 Unconfined compressive-strength test results

The compressive strength of the soil block cured in a sulfate solution (f'_{cu}) is determined by Equation 1.

$$f'_{cu} = \alpha f_{cu} \quad (1)$$

where α is the modified coefficient (Table 5) reflecting the corrosion degree and f_{cu} is the compressive strength of the block cured in pure water (i.e., when $\alpha = 1$).

The calculated unconfined compression strengths for the cemented soil blocks are shown in Figure 4. As demonstrated, the compressive strength decreases with the increase of the solution concentration. Generally, it increases with the corrosion time, except for the Na₂SO₄ solution with the high concentration (18.0g/L), where the strength is reducing to zero as the sample becomes broken.

Coefficients α greater than 1 are indicated in boldface in Table 5. For the α coefficients corresponding to 28 days of curing, we observed the following findings from Table 5.

Table 5. Modified coefficients (α) of cemented soils.

Concentration (g/L)	H ₂ SO ₄				MgSO ₄				Na ₂ SO ₄			
	3 d ¹	7 d	14 d	28 d	3 d	7 d	14 d	28 d	3 d	7 d	14 d	28 d
1.5	1.00	0.87	0.89	0.78	1.25	1.24	1.14	1.13	1.30	1.21	1.19	1.17
4.5	0.99	0.82	0.88	0.70	1.12	1.03	0.95	0.87	1.15	1.12	1.07	0.97
9.0	0.99	0.79	0.84	0.64	1.00	0.98	0.83	0.63	0.92	0.9	0.83	0.53
18.0	0.98	0.70	0.55	0.49	0.97	0.92	0.78	0.56	0.90	0.85	0.44	0

¹ d = days

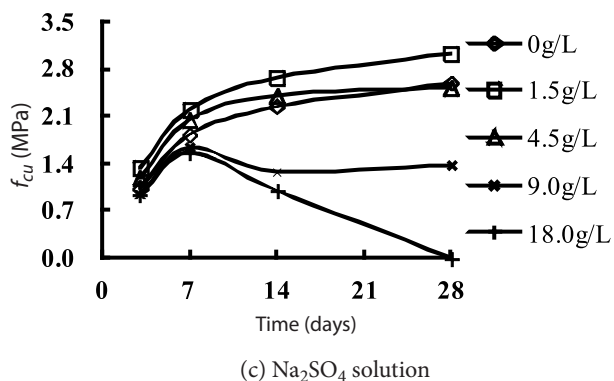
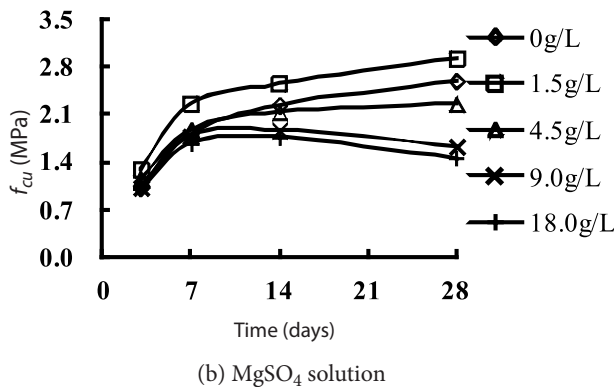
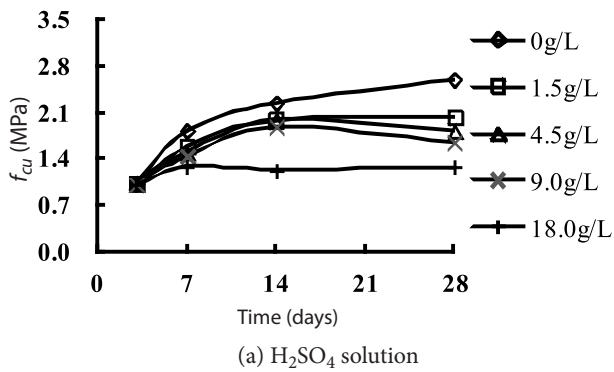


Figure 4. Relationship between the compressive strength (f_{cu}) of the cemented soils and the corrosion time.

- (1) For the MgSO₄ and Na₂SO₄ solutions with a 1.5g/L concentration, the coefficient α is greater than 1. This is a favorable environment as the compressive strength of the cemented soils will be increased.
- (2) For all the other concentrations of either solution the α coefficient is less than 1, indicating that the degree of corrosion is higher and the strength is reducing. The worst case occurs when the sample is cured in the Na₂SO₄ solution with a 18g/L concentration, where the strength becomes zero (i.e., $\alpha = 0$) due to broken samples (Table 5).

For safer, optimal, and more economical designs, it is suggested that the existing environmental condition of the cemented soils be taken into account when determining the foundation bearing capacity and settlement.

3.3 Relationship between the compressive strength (f_{cu}) and the ion concentration of solution (C)

- (1) f_{cu} versus C of SO₄²⁻

The relationship between f_{cu} and C of the SO₄²⁻ ion is shown in Figure 5. As indicated, the test data seem to be encompassed by a triangle with the slant described by $f_{cu} = -0.0008C + 4$. This signifies the close relationship between the compressive strength and the SO₄²⁻ concentration.

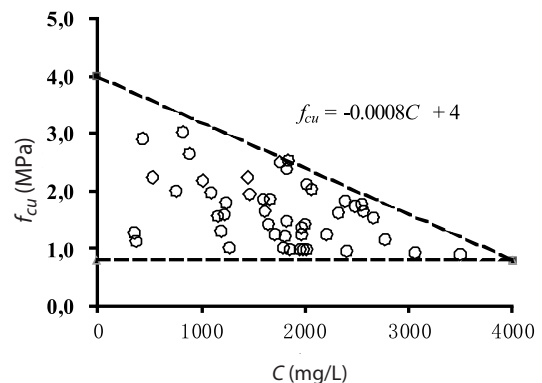


Figure 5. Relationship between f_{cu} and C of SO₄²⁻.

(2) f_{cu} versus the concentration of a positive ion (Mg^{2+} , H^+ , or Na^+)

The relation between f_{cu} and the positive ion concentration or the pH values is shown in Figure 6. It is clear that the compressive strength (f_{cu}) decreases with the increase of the Mg^{2+} concentration (C) of the $MgSO_4$ solution, nonlinearly expressed by $f_{cu} = -0.136\ln(C) + 2.1322$, where f_{cu} is in MPa and C is in mg/L (Figure 6a). f_{cu} decreases with the increase of the Na^+ concentration of the Na_2SO_4 solution linearly described by $f_{cu} = -0.0006C + 2$ (Figure 6c). Again, a close relationship between the compressive strength and the ion concentration is noted. f_{cu} increases with an increase of the pH value of the H_2SO_4 solution, also linearly represented by $f_{cu} = 0.0897V + 0.7372$, where V is the pH value (Figure 6b).

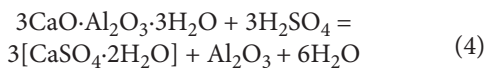
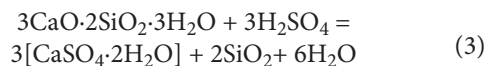
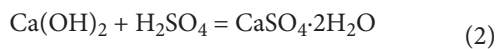
The above-derived mathematical expressions for f_{cu} could be useful for practical designs.

3.4 Analysis of the cemented soil phases and discussion of the corrosive mechanisms

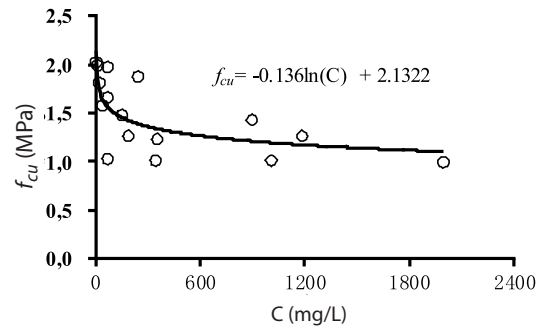
After 28 days of curing, XRD tests were performed for the corrosive powder samples that were taken from the $MgSO_4$, H_2SO_4 , and Na_2SO_4 solutions with a concentration of 18.0g/L. At the conclusion of the testing, the powder chemical products (phases) were analyzed using JADE5.0 software [22]. The analysis results are presented in Figures 7–9. As seen from the figures, the resulting chemical products are very different among the different sulfate solutions and pure water. Therefore, the chemical mechanism can be determined based on the X-ray diffraction (XRD) results and the chemical formulas.

(1) Corrosion mechanism for the cemented soil in the H_2SO_4 solution

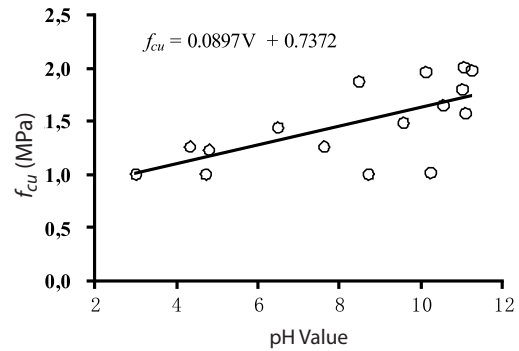
The main chemical reaction for the cemented soil in the H_2SO_4 solution is expressed by Equations (2)–(4).



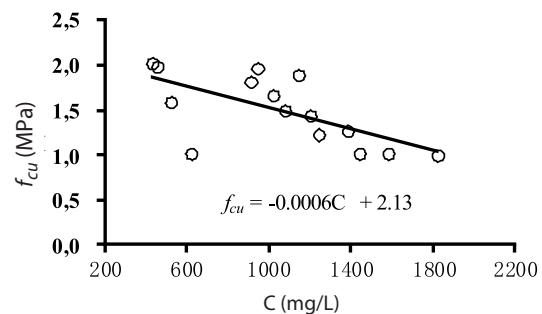
As indicated in the chemical formulas (2)–(4), H_2SO_4 reacts with $Ca(OH)_2$, $3CaO \cdot 2SiO_2 \cdot 3H_2O$ (C-S-H) and $3CaO \cdot Al_2O_3 \cdot 3H_2O$ (C-A-H), where H^+ participates actively and causes the cemented soil to form an unsteady structure. Therefore, the corrosion of the cemented soils in the H_2SO_4 solution is deemed as being a “resolving corrosion”.



(a) Compressive strength (f_{cu}) versus Mg^{2+} concentration (C).



(b) Compressive strength (f_{cu}) versus pH value (V).



(c) Compressive strength (f_{cu}) versus Na^+ concentration (C).

Figure 6. Relationship between the compressive strength (f_{cu}) and the positive ion concentration (C) or pH Value (V).

Figure 7 gives the corrosive products for the cemented soil in the H_2SO_4 solution with a 18.0g/L concentration. As shown, the peaks for the C-S-H ($3CaO \cdot 2SiO_2 \cdot 3H_2O$) phase diffraction are small and there is virtually no peak for either $Ca(OH)_2$ (C-H) or $3CaO \cdot Al_2O_3 \cdot 3H_2O$ (C-A-H) phase diffraction. For the H_2SO_4 solution with a high concentration of 18.0g/L, the cementing agent virtually does not function as intended. Based on the above results, the H_2SO_4 solution is acting in the acid state. These chemical reactions resolve the main cementing agents contained in the cemented soil, i.e., $Ca(OH)_2$, $3CaO \cdot 2SiO_2 \cdot 3H_2O$, and $3CaO \cdot Al_2O_3 \cdot 3H_2O$, and cause the surface peeling and strength reduction.

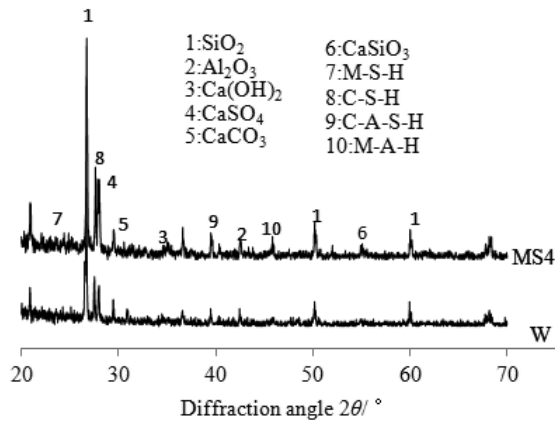
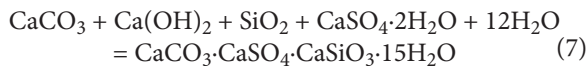
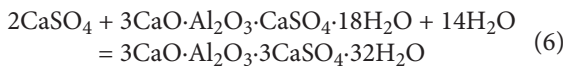
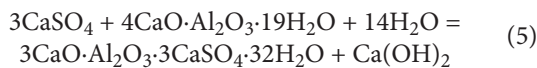


Figure 7. Chemical products in the H₂SO₄ solution (HS4) with a 18.0g/L concentration and in pure water (W).

Figure 7 also shows the apparently intense peaks for the C-A-S-H and CaSO₄ phase diffractions, where C-A-S-H means 3CaO·Al₂O₃·3CaSO₄·32H₂O and 3CaO·Al₂O₃·CaSO₄·18H₂O. Besides the resolving action, the dissociative SO₄²⁻ in the solution may take the following chemical reactions.



The effects of these reactions on the compressive strength are less significant for the cemented soil in the H₂SO₄ solution with a lower concentration as the ion H⁺ plays the main role. Those effects become more significant when the concentration is higher. The crystallizing resultants of 3CaO·Al₂O₃·3CaSO₄·32H₂O (C-A-S-H) and CaCO₃·CaSO₄·CaSiO₃·15H₂O (C-S-C-H) are apparently larger than the reactant. As such, their inflating force is greater than the sticking force in the cemented soil, and thus causes the cracking in the cemented soil block and the strength reduction. In conclusion, the H₂SO₄ solution results in a crystallizing corrosion in addition to the resolving corrosion.

(2) Corrosion mechanism for the cemented soil in the MgSO₄ solution

Figure 8 gives the corrosive products for the cemented soil in the MgSO₄ solution with a 18.0g/L concentration. From the figure, the peaks for the products C-A-S-H, M-A-H (MgO·Al₂O₃·H₂O), M-S-H (MgO·SiO₂·H₂O), and CaSO₄ appear more intense.

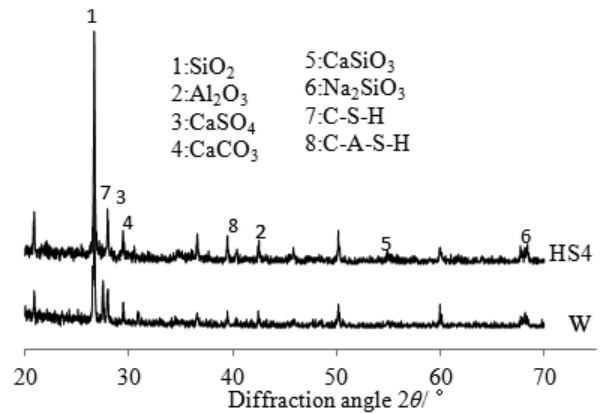
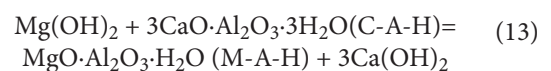
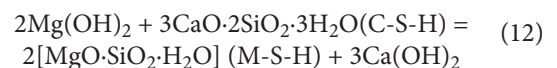
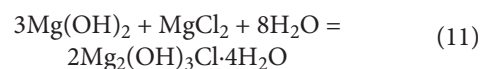
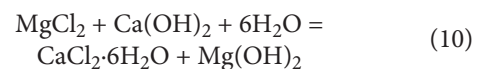
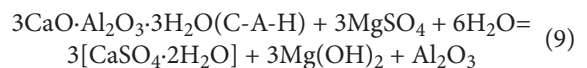
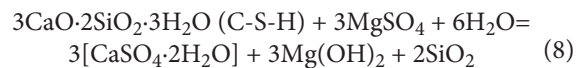


Figure 8. Chemical products in MgSO₄ solution (MS4) with 18.0g/L concentration and in pure water (W).

The main chemical reactions for the cemented soil in the MgSO₄ solution are expressed using Equations (8)–(13).



Equations (8) and (9) indicate a chemical reaction will take place to dissolve the main cementing agent (i.e., 3CaO·2SiO₂·3H₂O and 3CaO·2Al₂O₃·3H₂O), causing surface peeling for the cemented soil and strength reduction.

It has been well documented that the volumes for the resultants CaCl₂·6H₂O and Mg₂(OH)₃Cl·4H₂O [i.e., Equations (10) and (11)] are seven times those of Ca(OH)₂. So, the new products, CaCl₂·6H₂O and Mg₂(OH)₃Cl·4H₂O, can fill in the voids of the cemented soil. This is beneficial for the unconfined compressive strength of cemented soils when the mass of MgCl₂ is suitable and the new reactants (CaCl₂·6H₂O and Mg₂(OH)₃Cl·4H₂O) are small in each MgSO₄ solution. At a 1.5g/L concentration, the volume of CaSO₄·2H₂O resultants [from Equations (8) and (9)] is two times that of the Ca(OH)₂. CaSO₄·2H₂O is desirable for the

compressive strength of cemented soil as the mass of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is deemed suitable. This explains why the strength of the cemented soil cured in MgSO_4 solutions with a 1.5g/L concentration is greater.

However, the product of $\text{Mg}(\text{OH})_2$ may react with $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ (C-S-H) and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (C-A-H) if there is enough $\text{Mg}(\text{OH})_2$ in the MgSO_4 solution. The new reactants such as $\text{MgO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ (M-S-H) and $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (M-A-H) have poor coagulation, resulting in an unsteady structure and a reduced soil strength. Consequently, the corrosion of the cemented soil in the MgSO_4 solution is a resolving corrosion.

Besides the resolving action, the dissociative product $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ [produced by Equations (8) and (9)] may take the chemical reactions as expressed by Equations (5)–(7). The products $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 18\text{H}_2\text{O}$ (C-A-S-H) and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ may also have crystallizing corrosion. So, the corrosion for the cemented soil cured in the MgSO_4 solution is a combined resolving and crystallizing corrosion.

(3) Corrosion mechanism for the cemented soil in the Na_2SO_4 solution

Figure 9 gives the corrosive products for the cemented soil in the Na_2SO_4 solution with a 18.0g/L concentration. From the figure, the peaks for products C-A-S-H and CaSO_4 are more apparent. In addition to Equations (5)–(7), other chemical reactions for the cemented soil in the Na_2SO_4 solution include Equations (14)–(17).

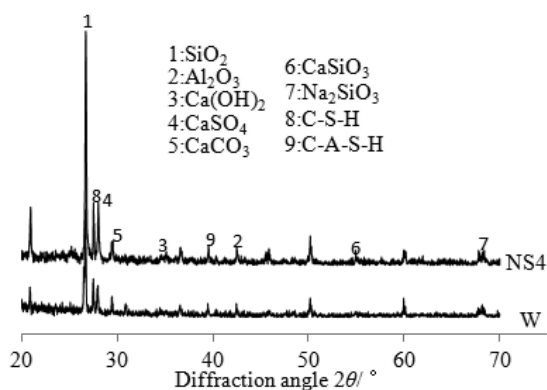
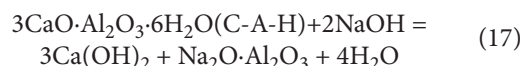
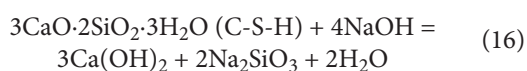
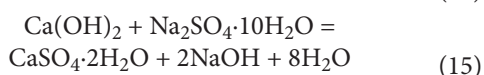
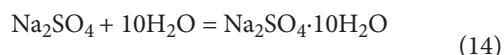


Figure 9. Chemical products in Na_2SO_4 solution (NS4) with 18.0g/L concentration and in pure Water (W).



For the Na_2SO_4 solution with a 1.5g/L concentration, with suitable mass of Na_2SO_4 , the new reactants (i.e., C-A-S-H and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) can fill the voids of the cemented soil and thus increase the unconfined compressive strength. This also explains why the strength of the cemented soil cured in the Na_2SO_4 solution with a lower concentration at 1.5g/L is larger.

For higher concentrations of the Na_2SO_4 solution, due to the excessive mass of Na_2SO_4 , the Na_2SO_4 will be combined with H_2O to produce the new crystallizing product of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ [Equation (14)]. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ tends to inflate with the cemented soil with C-A-S-H and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, the so-called “crystallizing inflation”, and reduces the strength.

One the other hand, Na_2SO_4 combined with $\text{Ca}(\text{OH})_2$ produces a new product, NaOH [Equation (15)]. NaOH may react with $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, when the amount of NaOH is enough in the cemented soil [Equations (16) and (17)]. Therefore, the sticking materials in the cemented soil will be decomposed and the new poorly coagulating reactants such as Na_2SiO_3 and $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$ will be formed, which dissolve the cemented soil. Hence, the corrosion of the cemented soil cured in the Na_2SO_4 solution is a combined dissolving and crystallizing corrosion.

In summary, the corrosion mechanism for the cemented soil in a H_2SO_4 or MgSO_4 solution is a composite type involving resolving and crystallizing. In addition, it is a composite type consisting of dissolving and crystallizing for the materials in a Na_2SO_4 solution.

4 CONCLUSIONS

Based on the results, the following conclusions can be drawn.

- (1) The sulfate solution changes the cement-soil block including peeling, size reduction, and cracking. The effect of the solution on the block increases with the increase of the concentration of the solution and the curing time.
- (2) The unconfined compressive strength of the cemented-soil block decreases with the increase of sulfate solution concentration and the curing time. The derived coefficients can be used to predict the modified compressive strength of cemented soil in various concentrations of corrosive solution.

- (3) The degree of the corrosion effect from the various solutions is in the descending order: $\text{Na}_2\text{SO}_4 > \text{MgSO}_4 > \text{H}_2\text{SO}_4$. When the SO_4^{2-} ion exists in a solution, the corrosion degree for the positive ions follows this descending order $\text{Na}^+ > \text{Mg}^{2+} > \text{H}^+$.
- (4) In terms of the corrosion mechanism for the cemented soil, the corrosion type is found to be a combined resolving and crystallizing for the H_2SO_4 and MgSO_4 solutions and a combined dissolving and crystallizing for the Na_2SO_4 solution.

Acknowledgement

This study was financially supported by the National Natural Science Foundation of China (Grant No. 51078253 & 51208333) and Natural Science Foundation of Shanxi Province (2014011036-1, 2014131019, TYUT2014YQ017, OIT2015). The opinions expressed in this paper are solely of the authors, however.

REFERENCES

- [1] Venkatarama-Reddy, B.V. and Jagadish, K.S. 1995. Influence of soil composition on the strength and durability of soil-cement blocks. *Ind. Con. J.* 69, 2, 517-524.
- [2] Walker, P.J. 1995. Strength, durability and shrinkage characteristics of cement stabilized soil blocks. *Cement. and Con. Comp.* 17, 4, 301-310.
- [3] Pei, X.J., Yang, G.C. 2000. Research on preventing cement erosion in marine soil. *J. Changchun Institute of Tech.* 9, 1, 12-14.
- [4] Shihata, S.A., Baghdadi, Z.A. 2001. Long-term strength and durability of soil cement. *J. of Mater. in Civil Eng.* 13, 3, 161-165.
- [5] Jiao, Z.B., Liu, H.L. 2005. Experimental study on cement soil strength in mucky-acid soil. *Chin. J. Rock and Soil Mech.* 26, 5, 57-60.
- [6] S. Koliass, V., Kasselouri-Rigopoulou, Karahalios, A. 2005. Stabilization of clayey soils with high calcium fly ash and cement. *Cem. Concr. Compos.* 27, 2, 301-313.
- [7] Ning, B.K., Chen, S.L., Liu, B. 2005. Fracturing behaviors of cemented soil under environmental erosion, *Chin. J. Rock and Soil Mech.* 24, 10, 1778-1782.
- [8] Ning, B.K., Jin, Chen S.J. 2006. Influence of erosive ions on mechanical properties of cemented soil. *J. Shenyang Univ. Technol.* 28, 2, 178-181.
- [9] Dong, X.Q., Bai, X.H., Zhao, Y.Q., Han, P.J. 2007. Study on electrical resistivity of soil-cement polluted by H_2SO_4 . *Chin. J. Rock and Soil Mech.* 28, 8, 1453-1548.
- [10] Dong, X.Q., Bai, X.H., Lv, Y.K. 2011. The influence of pH value and SO_4^{2-} concentration on strength of cemented soil. *Adv. Mater. Res.* 223, 5, 2006-2010.
- [11] Iyengar, S., Al-Tabbaa, A. 2008. Application of two novel magnesia-based cements in the stabilization/solidification of contaminated soils. *Geotech. Spec. Pub.* 177, 716-723.
- [12] Xing, H.F., Yang, X.M., Xu, C. 2000. Strength and microstructure of salt-rich soft soil improved by cement. *J. Tongji Univ.* 36, 12, 1606-1610.
- [13] Xing, H.F., Yang, X.M., Xu, C., Ye, G.B. 2009. Strength characteristics and mechanisms of salt-rich soil-cement. *Eng. Geol.* 103, 1, 33-38.
- [14] Zandieh, A.R., Yasrobi, S.S. 2010. Study of factors affecting the compressive strength of sandy soil stabilized with polymer. *Geotech. and Geologic. Eng.* 28, 5, 139-145.
- [15] Heineck, K.S., Lemos, R.G., Lautenschlager, C.E.R., Consoli, N.C. 2010 Behavior of vertical hydraulic barriers composed by sandy soil, bentonite and cement subjected to alkaline contaminants. *Geotech. Spec. Pub.* 199, 2462-2471.
- [16] Voglar, G. E., Lestan, D. 2011. Efficiency modeling of solidification / stabilization of multi-metal contaminated industrial soil using cement and additives. *J. of Hazard. Mat.* 192, 2, 753-762.
- [17] Liu, Z.P., Quan, Q.S., Liu, J.W., He, J. 2012. Study on durability of cement soil under brine erosion. *Adv. Mat. Res.* 446-449, 1, 1858-1863.
- [18] Yang, Y.Y., Wang, G.H., Xie, S.W. 2012. Effect of magnesium sulfate on the unconfined compressive strength of cement-treated soils. *J. of Test. and Eva.* 40, 7, 1-8.
- [19] Yang, Y.Y., Wang, G.H., Xie, S.W., Tu, X.M., Huang, X.G. 2013. Effect of mechanical property of cemented soil under the different pH value. *App. Clay Sci.* 79, No. 7, 19-24.
- [20] Gu, B.H., Gao, D.Z., Lin, Z.X., Li, S.Z. 2009. Chinese National Standard GB 50021-2009, Code for investigation of geotechnical engineering. Chinese building industry Press, Beijing.
- [21] Fan, D.E., He, J.Y., Yang, W.J. 2008. Chinese National Standard GB/T 50046-2008, Code for anticorrosion design of industrial constructions. Chinese Project Press, Beijing.
- [22] Wang, P.M., Xu, Q.W. 2005. Materials research methods. Chin. Science Press, Beijing.