Chlorine fixation by aluminate minerals in coastal chloride saline soil modification as subgrade material

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1 Introduction

Saline soil is widely distributed in coastal regions worldwide, where soft clay soils are common and high-quality subgrade materials are scarce. If saline soil is used as highway subgrade filler after modification, significant economic benefits can be achieved [1, 2]. In highway engineering, chloride saline soil refers to saline soil with a soluble salt content higher than 0.3% and a Cl^{-}/SO_4^{2-} content ratio greater than 2.0. The presence of soluble chloride salts makes the soil highly sensitive to environmental moisture. It readily absorbs water and may induce engineering distresses such as collapse, thereby leading to the degradation of road performance [3-5]. This has become one of the main factors restricting the application of coastal chloride saline soil as subgrade material. Scholars have carried out studies on the modification of chloride saline soil using inorganic binders, which have improved the road performance of the soil to a certain extent [6-8]. In studies on cement-based materials, it has also been found that chloride ions can react with the aluminum phases in cement clinker to form calcium chloroaluminate hydrates (Friedel's salt), thereby achieving chemical chlorine fixation [9, 10]. This provides a feasible approach to mitigating the engineering risks posed by soluble chloride salts.

This study focuses on the effectiveness, construction sensitivity, and mechanisms of chlorine fixation in modified soil. A road performance–oriented investigation is conducted on the composite modification of coastal chloride saline soil using lime and aluminate minerals. A multi-scale experimental approach is adopted, combining macroscopic tests, chemical analyses, and microstructural characterization. The aim is to provide experimental evidence and theoretical support for the engineering application of coastal chloride saline soil modified with aluminate mineral-based materials.

2 Materials and methods

The soil used was collected near the Binhai–Huai'an Expressway in Yancheng, Jiangsu Province, China. The soil consists mainly of silt (86.4%) and clay (12.7%), with a total soluble salt content of 1.075% (chloride ions accounting for 0.559%). Ordinary Portland cement, high-alumina cement, metakaolin, and lime were selected as modification materials. These materials are primarily composed of CaO, SiO_2, and Al_2O_3. To gain a deeper understanding of the chlorine fixation mechanism of aluminosilicate materials, tricalcium aluminate (C_3A) single mineral was prepared by a solid-phase reaction method. The primary components of the synthesized C_3A are CaO and Al_2O_3. The mix proportions of the prepared soil samples are shown in Table 1.

Table 1. Mix proportions of modified soil specimens.

Test group 1	Modifier content (by dry soil mass)	Test group 2	Modifier content (by dry soil mass)	Test group 3	Modifier content (by dry soil mass)
Untreated soil	–	A6	6% high-alumina cement	CA2	2% tricalcium aluminate
L3	3% lime	C6	6% ordinary Portland cement	CA3	3% tricalcium aluminate
A3	3% high-alumina cement	A3L3	3% high-alumina cement + 3% lime	CA4	4% tricalcium aluminate
C3	3% ordinary Portland cement	C3L3	3% ordinary Portland cement + 3% lime	CA6	6% tricalcium aluminate
M3	3% metakaolin	M3L3	3% metakaolin + 3% lime	CA3L3	3% tricalcium aluminate + 3% lime

Road performance tests were conducted in accordance with relevant specifications over samples of Test group 1 and Test group 2. The experimental program included the compaction test, the California Bearing Ratio (CBR) test, and the unconfined compressive strength (UCS) test. Microstructural tests included X-ray diffraction (XRD) and scanning electron microscopy (SEM).

The specimens were cured under standard conditions with a relative humidity of 95% and a temperature of 20 ± 2 °C. To investigate the temperature sensitivity, selected groups were additionally cured at 10 °C and 30 °C.

The chloride ion content in the soil filtrate was determined for samples in Test group 1, Test group 2, and Test group 3 using the silver nitrate titration method. The chloride ion fixation rate, P, was calculated according to Equation (1).

$$P = [(C_0 - C_1)/C_0] * 100\% \quad (1)$$

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where P is the chloride ion fixation rate (%); C_0 is the initial chloride ion content of the chloride saline soil (g/kg); and C_1 is the chloride ion content of the modified chloride saline soil after curing to a specified age (g/kg).

Macroscopic tests (compaction, CBR and UCS) were used to directly evaluate the improvement in engineering properties, while microstructural analyses (XRD and SEM) were conducted to identify the formation of reaction products (e.g., Friedel's salt). At the chemical level, the chloride ion fixation rate test quantifies the effectiveness of this process.

3 Results and discussion

3.1 Improvement in road performance of modified soil

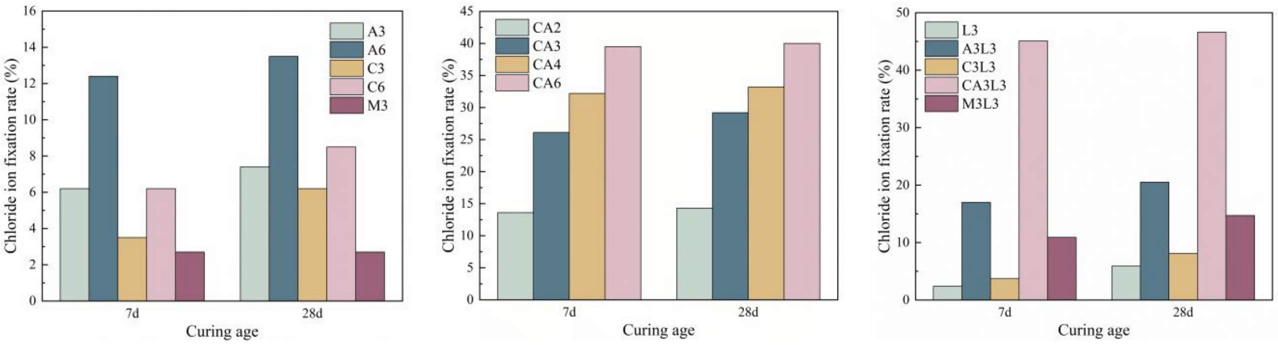
The results of the compaction tests, CBR tests, and unconfined compressive strength tests for soil modified with lime and aluminate minerals are presented in Table 2. Modification with lime combined with ordinary Portland cement or high-alumina cement effectively improved the mechanical properties of the soil, whereas the effect of metakaolin was not significant. At a compaction degree of 96%, the CBR values of all specimens exceeded the specified requirement of 8%.

Table 2. Test results of road performance.

Test group	Maximum dry density /(g/cm^3)	Optimum water content /%	Soaked CBR (4d) /%	UCS after 7d curing /MPa	UCS after 28d curing /MPa	UCS after 90d curing /MPa
Untreated soil	1.79	16.6	11.7			0.41
L3	1.80	17.0	177	1.48	1.78	1.94
A3	1.78	16.8	199	1.15	1.12	1.10
C3	1.80	16.9	183	1.29	1.62	1.79
M3	1.79	15.2	18	0.43	0.45	0.47
A6	1.72	18.2	201	1.71	1.52	1.51
C6	1.73	17.9	190	1.53	1.89	1.99
A3L3	1.72	17.2	181	1.64	1.95	2.04
C3L3	1.71	17.4	239	1.85	2.22	2.54
M3L3	1.66	18.2	168	1.27	1.55	1.78

3.2 Chlorine fixation of modified soil

Figure 1 shows the chloride ion fixation rates of modified soil after curing for different ages. At the same curing age, the chloride ion fixation rate increased with increasing aluminate mineral content. Using tricalcium aluminate (C_3A) single mineral as a modifier more clearly demonstrates the chlorine fixation effect of aluminate minerals on chloride saline soil. Within the dosage range of 3%–6%, the soil modified with 6% C_3A exhibited the best chlorine fixation efficiency, reaching 40% after 28 days of curing. The chloride ion fixing capacity of High-alumina cement was second only to that of the C_3A single mineral, followed by ordinary Portland cement. The chlorine fixation effect of metakaolin modification was not significant.



(a) (b) (c)

Figure 1. Chlorine fixation efficiency of: (a) aluminate mineral–modified soil; (b) tricalcium aluminate–modified soil (c) lime–composite modified soil.

The results of the chloride ion fixation rates of soils modified with the addition of lime are shown in Figure 1c. The incorporation of lime further enhanced the chlorine fixation performance. After 28 days of curing, the chlorine fixation rate of soil modified with 3% lime + 3% C_3A reached 46.6%, which was superior to that of soil modified with 6% C_3A. This is because lime provides an alkaline environment that promotes the dissolution of aluminum phases in clay minerals. In addition, lime supplies Ca^{2+} to the system, thereby promoting the reaction between aluminates and chloride ions.

3.3 Microstructural analysis of modified soil

XRD analysis was conducted and the test results are shown in Figure 2. Compared to the unmodified soil, the other two modified soil groups exhibited characteristic diffraction peaks related to Friedel's salt at approximately 11.2°.

Figure 3 shows SEM images of the unmodified soil and the soil modified with 6% C_3A. The soil particles in the unmodified soil are loosely arranged, with large and numerous pores. In the modified soil, Friedel's salt crystals measuring 2~3 μm in size, exhibit a hexagonal platy crystal morphology. The Friedel's salt crystals effectively fill the pores and cement the soil particles, which can provide a reinforcing effect on the subgrade soil.

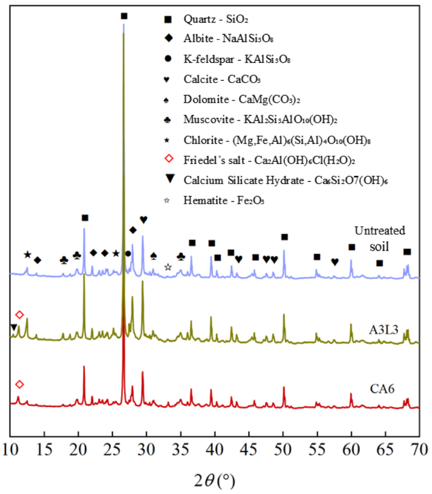


Figure 2. XRD results.

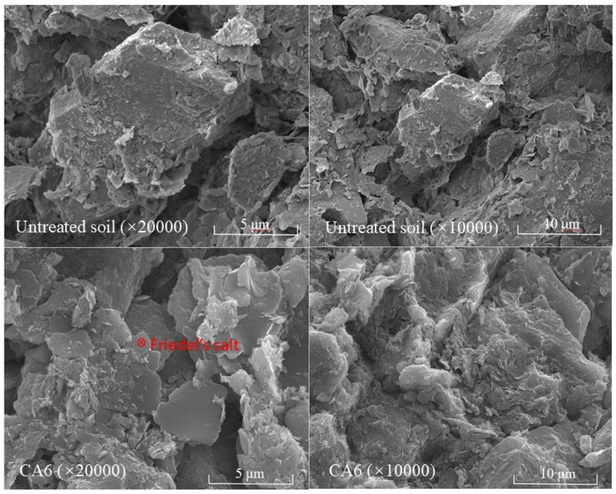
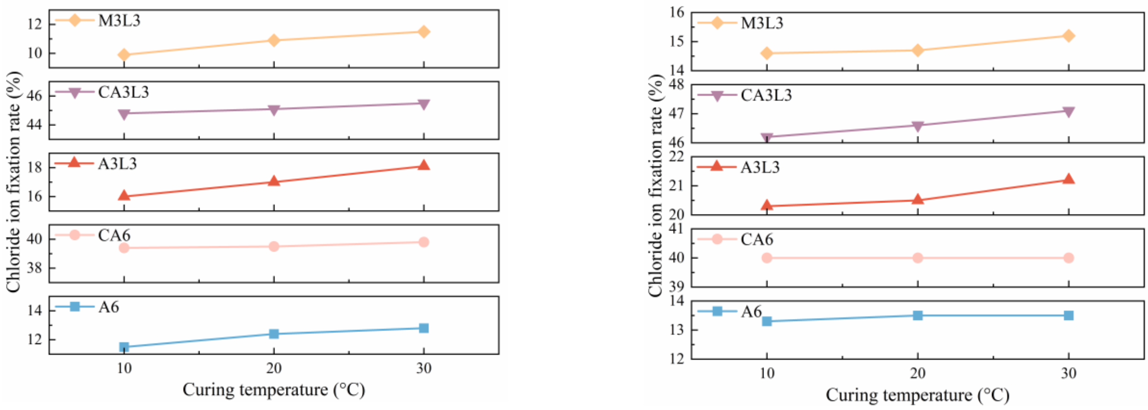


Figure 3. SEM images.

3.4 Construction and environmental sensitivity of chlorine fixation in modified soil

To investigate the sensitivity of chlorine fixation efficiency of modified soil to construction and environmental conditions, the chloride ion fixation rates were measured under different curing temperatures and degrees of compaction.

Figure 4 shows the chlorine fixation of modified soil when the curing temperature was 10 °C, 20 °C and 30 °C. Within this temperature range, an increase in temperature enhances chlorine fixation efficiency of aluminates to a certain extent. For soil modified with aluminate minerals, this enhancement is mainly observed at the early stage of the reaction. In the later curing stage, the influence of curing temperature of lime-amended modified soil is more pronounced.

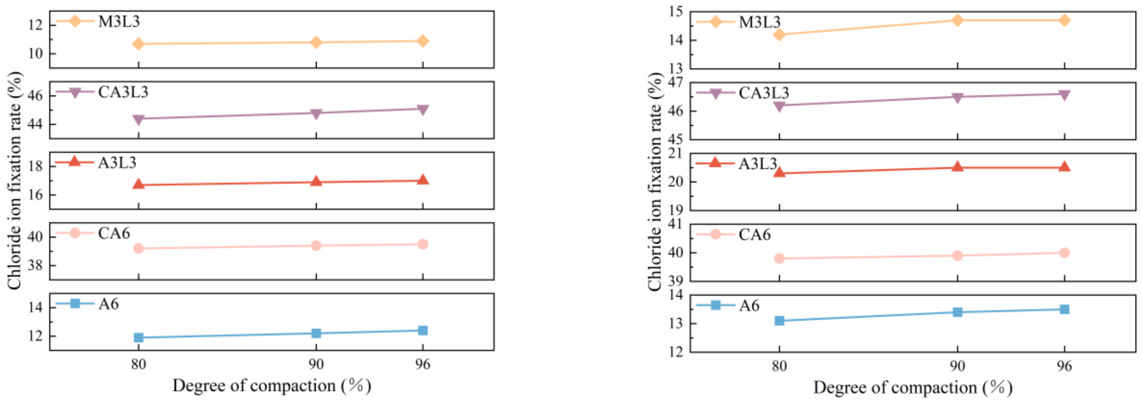


(a) (b)

Figure 4. Effect of curing temperature on the chlorine fixation performance of modified soil: (a) curing for 7 days; (b) curing for 28 days.

Figure 5 shows the variation trend of the chlorine fixation of modified soil when the degree of compaction was 96%, 90% and 80%. By observing the trend, the following conclusion is drawn. Within the compaction degree range of 80–96%, the chlorine fixation process shows low sensitivity to the degree of compaction.

Existing studies consider compacted subgrade soil (containing clay particles) to exhibit an aggregate skeleton structure, in which the structural units are aggregate particles [11]. The macroscopic structure of compacted chloride saline soil is also regarded in this manner. Its pore structure consists of micropores within aggregate particles and interparticle pores between aggregates. Soluble chloride salts are distributed in both macropores and micropores. A reduction in soil porosity increases the contact probability between aluminum phases and Cl^-, thereby promoting the formation of Friedel's salt. However, the degree of compaction has a limited effect on chlorine fixation, indicating that chlorine fixation process by aluminate minerals mainly occurs within soil aggregates.



(a) (b)

Figure 5. Effect of compaction degree on the chlorine fixation performance of modified soil: (a) curing for 7 days; (b) curing for 28 days.

4 Conclusion

This study investigated the road performance and chlorine fixation behavior of coastal chloride saline soil modified with lime and aluminate minerals from a multi-scale perspective. The main conclusions are as follows:

1. Composite modification with lime and High-alumina cement or ordinary Portland cement can improve the mechanical properties of chloride saline soil, thereby enhancing its road performance including CBR and UCS.
2. Aluminate minerals can effectively fix chloride ions. Tricalcium aluminate (C_3A) chemically combines with chloride ions in the soil to form Friedel's salt, thereby achieving chlorine fixation. The chloride ion fixation rate of the modified soil increases with a higher dosage of aluminate mineral content. Among the tested materials, the modified soil containing tricalcium aluminate single mineral exhibits the best chlorine fixation efficiency, followed by High-alumina cement and ordinary Portland cement, while the chlorine fixation effect of metakaolin modification is not significant.
3. The incorporation of lime further enhances the chlorine fixation performance of the modified soil.
4. Within the curing temperature range of 10–30 °C, an increase in temperature can promote the chlorine fixation efficiency to a certain extent.
5. Within the compaction degree range of 80–96%, the chlorine fixation process shows low sensitivity to the degree of compaction, further indicating that chloride ion fixation mainly occurs within soil particle aggregates.

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