

Article



Experiment and Mechanism Analysis on the Solidification of Saline Dredger Fill with Composite Slag Solidifying Agent: A Case Study in Caofeidian, China

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Abstract: Most areas of Caofeidian (Tangshan Caofeidian New District in Hebei Province, China) were formed by land reclamation, where the dredger fill has a high water content and a high salt content. The solidification of Caofeidian's dredger fill is difficult because of salinisation, as well as environmental and economic factors. This article proposes a composite slag solidifying agent. The optimal proportion of various additives was determined by an unconfined compression test and orthogonal design. Next, a microanalysis was carried out by SEM and XRD tests to characterise the solidification mechanism of the composite slag solidifying agent. The results reveal that the composite slag solidifying agent can substantially improve the unconfined compressive strength of Caofeidian's saline dredger fill by imparting a good microstructure: a compact overall structure was obtained and few voids were observed in the solidified soil. The optimal proportion was determined as 10% slag + 1.0% quicklime + 0.8% sodium silicate + 1.5% gypsum powder. In addition, the composite slag solidifying agent can effectively reduce the content of soluble salts in saline dredger fill and substantially improve the engineering characteristics of solidified soil.

Keywords: saline dredger fill; composite solidifying agent; unconfined compression test; SEM; XRD

1. Introduction

Most areas of Caofeidian (Tangshan Caofeidian New District in Hebei Province, China) were formed by land reclamation. The reclamation area has reached 380 km². The common method of shallow foundation treatment in Caofeidian area is the squeezing of silt with broken rocks. This can straightforwardly damage underground pipelines. Furthermore, a large amount of broken rocks is required, and these need to be transported from places that are 200 km away. Both the breaking of mountains to extract stones or rocks and the long-distance transport are hazardous to the environment and uneconomical. In addition, the dredger soil in this area was extracted from the offshore sand, which has a large salt content. The groundwater level in this area is high, and the seawater erosion is significant, which results in severe soil salinization. As a result, the engineering characteristics of dredger soil, such as short consolidation time, high water content, and salinization, have significantly hindered the construction and development of the Caofeidian area project.

Recently, soil solidifying agents have been developed and widely used in the construction of infrastructure such as ports, roads, and water conservancy facilities because of their remarkable properties, low prices, and good treatment effects [1].

Lime and cement were the earliest solidifying agents used by humans and are widely applied worldwide. These agents have been applied and studied by many researchers. De Brito Galvao et al., Elhagwa et al., and Nafi Abdel et al. used lime to solidify clay [2–4]. Rajasekaran et al., Rajasekaran, and McCarthy et al. used lime to strengthen sulphated coastal



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). clay [5–9]. Miller et al. conducted experimental research (on-site and laboratory) on cement kiln dust (CKD) as a soil stabilizer [10]. Chan et al. studied dredged marine clay solidified with cement and fly ash and other binders [11]. In addition, certain new solidifying materials have been examined by a few researchers: Bell investigated the use of lime-combined PFA (pulverised fuel ash) and cement-combined PFA to solidify clay soil [12]. Attom et al. proposed the use of burned olive waste as a new soil solidifying agent [13].

However, it has been demonstrated that conventional solidifying agents have a low solidifying effect on coastal dredger soils with high water content and salinization. Sabry et al. observed that the strength of cement-solidified soil increases slowly in a saline environment over the long term, and that durability is reduced significantly owing to the corroding effect of salt [14]. Omar Saeed et al. demonstrated that the use of lime as solidifying agent cannot effectively improve the strength and durability of dry saline soil [15]. Therefore, a few researchers improved conventional solidifying agents with additives for saline environments. For example, Wild et al. used ground granulated blast-furnace slag (GGBS) to replace part of the lime to solidify sulphate-containing Kimmeridge clay [16]. The results revealed that the strength of solidified clay soil was improved significantly. Hossain et al. proposed that industrial wastes such as lime, volcanic ash, and their mixtures are good solidifying materials for saline clay soil [17]. Kamon et al. proposed that industrial waste slag mixed with aluminium slime can enhance the early strength of saline soil [18].

Simultaneously, X-ray diffraction (XRD), scanning electron microscopy (SEM), and other microscopic test methods have been applied in different research studies to clarify the mechanism of saline soil solidification and to select good solidifying agents. For example, based on these microscopic analyses, Suryavanshi et al. discussed the formation mechanism of Friedel's salt ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$) and the analogues in C₃Arich ($3CaO \cdot Al_2O_3$) cement soil [19]. Huang et al. considered that the expansion of AFt ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) plays a dual role: it can simultaneously fill pores to solidify soil and destroy the solidified soil structure formed by calcium silicate hydrate (CSH) [20].

According to previous researches, soil-solidifying agents are used widely. However, the conventional method of using a single solidifying agent has a low solidifying effect on saline soil. Composite solidifying agents containing industrial waste and other cementing materials have a better solidifying effect on saline soil. Nevertheless, the solidifying mechanism has been studied inadequately, and there is an urgent need to investigate the components and their proportions for composite solidifying agents for saline dredger fill. The verification of certain hydration products (such as CSH, AFt, and Friedel's salt) during the solidification of this soil is also highly worthwhile.

Therefore, in the present study, a composite solidifying agent (slag is used as the main solidifying agent and sodium silicate, quicklime, and gypsum powder are used as additives) is proposed to improve the strength of the Caofeidian saline dredger fill. The optimal mixture ratio of the composite solidifying agent was determined by unconfined compression tests. Finally, the hydration products and solidifying mechanism of the composite slag solidifying agent were investigated based on SEM scanning and XRD diffraction tests.

2. Materials Studied

2.1. Caofeidian Dredger Fill

Caofeidian belongs to Tangshan City, Hebei Province, China. It is located on the southern coast of Tangshan and in the centre of Bohai Bay (Figure 1). The elevation of the reclamation area is approximately 4.5 m, and the area is flat overall. Based on the site survey (20 m depth), it can be stated that it mainly contains silty sand, silt, and silty clay layers formed by quaternary Holocene sedimentary layers (Q4m), except the surface dredge fill (Q4ml).



Figure 1. Location of Caofeidian.

The dredge fill material studied in the present work is extracted from a site that is 50 m north of Caofeidian Station $(39^{\circ}2'13'' \text{ N}, 118^{\circ}30'34'' \text{ E})$. The soil is extracted from a depth of approximately -2.0--1.5 m. The material is representative because it only has a period of self-weight consolidation without reinforcement. The geotechnical parameters of the material studied are determined following the Chinese Standard JTG E40-2007, as shown in Table 1. The components of soluble salt are calibrated following the Chinese Standard GB/T 50123, as presented in Table 2.

Table 1. Geotechnical parameters of Caofeidian dredger fill.

Material	Natural Moisture Content	Optimum Moisture Content	Maximum Dry Density	Gs	Liquid Limit	Plastic Limit	Plasticity Index	Liquid Index
	(%)	(%)	(g/cm ³)	(g/cm ³)	(%)	(%)	N/A	N/A
Caofeidian dredger fill	26.1	16.4	1.64	2.70	26.29	13.6	12.69	0.88

Table 2. Components of soluble salt of Caofeidian dredger fill.

	Ani	ions			Cat				
CO32-	HCO ₃ -	SO4 ²⁻	Cl-	Ca ²⁺	Mg ²⁺	K+	Na ⁺	Total Solu	ible Salt
(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(%)
0	304.9	1893.0	5972.9	297.4	3181.2	205.3	2288.5	13035.0	1.3

Table 1 shows that the natural water content of the Caofeidian dredger fill is 26.1% (which is close to the liquid limit), and its plastic index is 12.69. Therefore, the material can be classified as low-liquid-limit clay based on ASTM 2487 (classification of fine-grained soil) [21]. According to Table 2, it can be stated that Na⁺ and Mg²⁺ are the main cations and Cl⁻ and SO₄²⁻ are the main anions in the soluble salt, and that the main soluble salts are NaCl, MgCl₂, and sulphate. The total salt content of the Caofeidian dredger fill is 1.3%.

2.2. Solidifying Agents

2.2.1. Main Solidifying Agent

The slag (granulated blast furnace slag (GBFS)) powder is used as the main solidifying agent in this work. Its main chemical composition is shown in Table 3. This white powder

has a specific surface area and density of $429 \text{ m}^2/\text{kg}$ and 2.9 g/cm^3 , respectively. The 7 day and 28 day activity indexes are 83% and 98%, respectively.

Table 3. Proportion of chemical composition of slag.

Chemical Composition	SiO ₂	Al_2O_3	CaO	MgO	Others
Mass percentage (%)	35–50	15–20	20–30	5–15	Negligible

2.2.2. Additives

As the main solidifying agent, slag exhibits certain activity. However, it does not easily achieve hydration reactions at ambient temperature. Hence, alkaline materials (sodium silicate and quicklime) and sulphate (gypsum powder) were used to activate the slag in this study. NaOH generated by sodium silicate can dissolve the surface vitreum of slag and promote the formation of CSH colloid. The colloid is capable of filling the pores of soil and thereby, increasing its density. The effects of the water absorbency, exothermicity, and expansibility of quicklime facilitate soil hardening. In addition, the generated Ca(OH)₂ contributes to the formation of CSH colloid and calcium aluminate hydrate (CAH) colloid. Gypsum powder can promote the hydration of slag. Meanwhile, SO_4^{2-} reacts with calcium aluminate hydrate to yield AFt, which can fill the pores of soil effectively and form the spatial network structure required to enhance soil stability.

3. Unconfined Compression Test

3.1. Sample Preparation and Test Procedure

An unconfined compression test was used to investigate the effect of the mixture ratio of the solidifying agent on the strength of the solidified Caofeidian dredger fill. The mix proportion design for the unconfined compression test is presented in Table 4. The 10% slag was used as the main solidifying agent, and three additives (sodium silicate, quicklime, and gypsum powder) at different content levels were applied to two approaches for sample preparation: single-additive and composite-additive. The orthogonal design is applied in the composite additive method.

Table 4. Proportion design for unconfined compression test.

Number	Test Type	Slag (%)	Quicklime (%)	Sodium Silicate (%)	Gypsum Powder (%)
A0		0	0	0	0
A1		10	0.5 (Level-1)	0	0
A2		10	1.0 (L-2)	0	0
A3		10	1.5 (L-3)	0	0
A4	Single additive	10	0	0.6 (L-1)	0
A5	Single-additive	10	0	0.8 (L-2)	0
A6		10	0	1.0 (L-3)	0
A7		10	0	0	0.5 (L-1)
A8		10	0	0	1.0 (L-2)
A9		10	0	0	1.5 (L-3)
A10		10	0.5 (L-1)	0.6 (L-1)	0.5 (L-1)
A11		10	0.5	0.8 (L-2)	1.0 (L-2)
A12		10	0.5	1.0 (L-3)	1.5 (L-3)
A13		10	1.0 (L-2)	0.6	1.0
A14	Composite-additive	10	1.0	0.8	1.5
A15		10	1.0	1.0	0.5
A16		10	1.5 (L-3)	0.6	1.5
A17		10	1.5	0.8	0.5
A18		10	1.5	1.0	1.0

The soil was prepared with a water content of 16.4%. Next, the different types and proportions of solidifying agents were mixed well with wet soil. Finally, the soil samples were compacted in a cylindrical mould with a dry density of 1.63 g/cm³ (99% of maximum dry density).

Subsequently, the sample was demoulded and cured in a curing chamber at a temperature of 20 ± 2 °C and humidity of 90%. After 7 and 28 days of curing, unconfined compression tests were carried out to obtain the 7 day and 28 day compressive strength, respectively, of the solidified Caofeidian dredger fill. The instrument used in the test was an electric limestone unconfined pressure tester (Tianjian, China). The test was controlled to a speed of 1 mm/min and terminated when the sample failed.

3.2. Test Results

3.2.1. Single-Additive

The results for the unconfined compressive strength of solidified Caofeidian dredger fill with different single additives are presented in Table 5 and Figure 2.

Table 5. Test results of single-additive samples.

Number	Unconfined Compressive Strength (kPa)					
Nulliber	7 d	28 d				
A0	18	41				
A1	475	1550				
A2	890	2015				
A3	672	1406				
A4	36	288				
A5	99	389				
A6	201	505				
A7	45	121				
A8	54	135				
A9	59	157				

The 7 day and 28 day compressive strength of unsolidified Caofeidian dredger fill were 18 kPa and 41 kPa, respectively. Figure 2a illustrates the 7 day and 28 day compressive strength with quicklime as the single additive. It can be stated that the strength first increased and then decreased with the increase in quicklime content: the strength increased for quicklime content between 0% and 1% and decreased for quicklime content higher than 1%. The maximum 7 day and 28 day compressive strength reached 890 kPa and 2015 kPa, respectively, with 1% quicklime.

Figure 2b,c present the 7 day and 28 day compressive strength with sodium silicate and gypsum powder, respectively, as single additives. It can be stated that the strength increased with the increase in the content of sodium silicate and gypsum powder. However, the final increase in strength was negligible compared with the result for quicklime as the single additive: the maximum 7 day and 28 day compressive strength reached 201 kPa and 505 kPa, respectively, with 1% sodium silicate, and 59 kPa and 157 kPa, respectively, with 1.5% gypsum powder.





Figure 2. Unconfined compressive strength of samples with different single additives: (**a**) quicklime; (**b**) sodium silicate; (**c**) gypsum powder.

3.2.2. Composite-Additive

The results of the unconfined compression test performed on solidified Caofeidian dredger fill with composite additives are presented in Table 6.

Table 6. Test results of composite-additive samples
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Number	Unconfined Compressive Strength (kPa)				
Number	7 d	28 d			
A10	1483	2764			
A11	1981	3033			
A12	1681	2870			
A13	1886	3200			
A14	2007	3370			
A15	1907	3020			
A16	1827	2401			
A17	1680	2640			
A18	1460	2374			

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Table 7 presents the range analysis of the orthogonal test. T_i is the sum of the strength at Level *i*, and t_i is the average strength. The range is calculated as $t_{i-max}-t_{i-min}$, which indicates the degree of influence of the three additives on the unconfined compressive strength. Based on the results, it can be stated that quicklime was the key additive. It had the maximum range of values for both 7 day and 28 day strength. It was followed by sodium silicate and, next, by gypsum powder. In addition, the optimal proportion scheme could be obtained based on strength tests and orthogonal analysis as 10% slag, 1% quicklime, 0.8% sodium silicate, and 1.5% gypsum powder. The unconfined compressive strength of the solidified Caofeidian dredger fill with the optimal proportion attained 2007 kPa in 7 d and 3370 kPa in 28 d. These results were slightly lower than or close to the results from [22], in which a different slag composite curing agent was applied to the Caofeidian coastal saline soil.

Table 7. Range analysis of orthogonal test.

Т		7d			28d	
	Quicklime	Sodium Silicate	Gypsum Powder	Quicklime	Sodium Silicate	Gypsum Powder
T_	5145	5200	5070	8667	8365	8424
T_2	5800	5668	5327	9590	9043	8607
T ₃	4967	5048	5515	7415	8264	8641
t ₁	1715	1733	1690	2889	2788	2808
t ₂	1933	1889	1776	3197	3014	2869
t ₃	1656	1683	1838	2472	2755	2880
Range	277	206	148	725	259	72
Optimal proportion	1.0%	0.8%	1.5%	1.0%	0.8%	1.5%
influence factor	Quicklime > Se	odium silicate	> Gypsum powder	Quicklime > Se	odium silicate >	Gypsum powder

4. Microanalysis

4.1. Sample Preparation and Test Procedures

As presented above, the composite additive with the optimal proportion solidified the Caofeidian dredger fill effectively. A microanalysis was carried out by SEM test and XRD test to characterise the mechanism of solidification for the composite additives. For comparison, the unsolidified soil sample and solidified soil samples with single additives were also investigated. The proportion design for the microanalysis tests is presented in Table 8.

Table 8. Proportion design for microanalysis.

		Proportion of Solidifying Agent/%						
Number	Description	Slag (%)	Gypsum Powder (%)	Sodium Silicate (%)	Quicklime (%)			
B1	Unsolidified soil	0	0	0	0			
B2	Slag + Gypsum powder	10	1.5	0	0			
B3	Slag + Sodium silicate	10	0	0.8	0			
B4	Šlag + quicklime	10	0	0	1			
B5	Slag + all	10	1.5	0.8	1			

For the SEM test, a $2 \times 2 \times 2$ mm³ cubical core sample was extracted from the sample of unconfined compression test after 28 days of curing. The gold sputtering coating treatment was applied to the cubical sample in vacuum before the test. An SU8010 cold-field emission scanning electron microscope (Hitachi, Japan) was used in the test. Next, an incidental energy-dispersive spectrometer (EDS) analysis was applied to a selected representative region, as shown in Appendix A.

For the XRD test, the core sample for the unconfined compression test after 28 days of curing was extracted and ground into powder (<360 mesh). Next, a SmartLab X-ray polycrystalline diffractometer (Rigaku, Japan) was applied to perform the XRD pattern analysis.

4.2. *Results and Analysis* 4.2.1. Unsolidified Soil

Figure 3a presents the microscopy image of unsolidified soil. It can be stated that the particles of unsolidified soil were different in size, disturbed, and block-shaped. The point-point and point-surface contacts between particles were the main contact mechanism without a structural link. Large voids between particles were apparent and distributed widely. In addition, the unsolidified soil was prepared with a maximum dry density of 1.63 g/cm³. This implies that the microstructure of the unsolidified soil was significantly loose and that its strength was low, as determined by the unconfined compression test described above. Figure 3b presents a finer image of the particles. It is evident that the surfaces of the particles were relatively smooth, without crystal production. Figure 4 presents an X-ray powder diffractogram of unsolidified soil. Combining the EDS and XRD analysis, it demonstrates that the main substances were quartz (SiO₂) and albite (Na₂O·Al₂O₃·6SiO₂).



Figure 3. Microscopy images of unsolidified soil. (a) 100 µm scale; (b) 10 µm scale.



Figure 4. X-ray powder diffractogram of unsolidified soil.

4.2.2. Solidified Soil with Slag and Gypsum Powder

Figure 5a presents the microscopy images of the solidified soil with slag and gypsum powder. It can be observed that compared with unsolidified soil, the soil structure was compact and that the soil grains varied in shape and size. The contacts between the soil particles were mainly point–point, point–surface, and surface–surface. The surface of the soil particles was non-uniform, and there were many voids. The shape and size of the voids differed, and few overhead voids were observed. Based on Figure 5b, it can be stated that a few crystals are formed on the surface of the grain. The crystals were mainly shaped as strips and fine particles.



Figure 5. Microscopy images of solidified soil with slag and gypsum powder. (**a**) 100 μ m scale; (**b**) 10 μ m scale.

The X-ray powder diffractogram is shown in Figure 6. Combining the EDS and XRD analysis, it can be demonstrated that the main crystalline phase substances were quartz (SiO₂), albite (Na₂O·Al₂O₃·6SiO₂), and gypsum (CaSO₄·2H₂O). Unlike in the unsolidified soil, CaSO₄·2H₂O was the new crystalline substance generated from the hydrolysis of gypsum powder (anhydrous gypsum: CaSO₄) as follows:

$$CaSO_4 + 2H_2O = CaSO_4 \cdot 2H_2O \tag{1}$$



Figure 6. X-ray powder diffractogram of solidified soil with slag and gypsum powder.

CaSO₄·2H₂O generally appeared as fine needle-shaped and columnar crystals (as shown in Figure 5b), which contributed toward increasing the compressive strength to a certain extent.

4.2.3. Solidified Soil with Slag and Sodium Silicate

As shown in Figure 7a, compared with the results for the gypsum powder, a denser structure could be obtained in the soil solidified with slag and sodium silicate. The distribution of massive particles was relatively compact. The contacts between the soil particles were mainly point–surface and surface–surface, and the contact area increased. A certain amount of void and colloidal filler was apparent. In addition, Figure 7b reveals that a certain amount of crystals (strips and needles) formed on the surfaces of the grains, which filled the void and increase the contact between the grains. This was the main reason for the improvement in strength for the solidified soil with slag and sodium silicate.



Figure 7. Microscopy image of solidified soil with slag and sodium silicate. (**a**) 100 μ m scale; (**b**) 10 μ m scale.

The X-ray powder diffractogram is shown in Figure 8. Combining the EDS and XRD analyses, it can be demonstrated that the main substances in the crystalline phase were quartz (SiO₂), albite (Na₂O·Al₂O₃·6SiO₂), anorthite (CaO·Al₂O₃·2SiO₂), and CSH (CaO·SiO₂·H₂O). Quartz and albite were crystalline minerals that pre-existed in the dredger soil, and anorthite and CSH were new reaction products. During the solidification, NaOH from Na₂SiO₃ hydrolysis increased the pH value of the sample. In the alkaline environment, CaO and other vitreous structural substances in the soil and slag dissolved straightforwardly to yield Ca²⁺. Ca²⁺ is conveniently replaced with Na⁺ from sodium silicate (Na₂SiO₃) to form CSH. In this manner, CSH formed continuously, and the OH⁻ (alkaline environment) remained in the soil to maintain the circulation of the solidification.



Figure 8. X-ray powder diffractogram of solidified soil with slag and sodium silicate.

4.2.4. Solidified Soil with Slag and Quicklime

Figure 9 presents the microscopy image of solidified soil with slag and quicklime. A dense and almost self-contained structure was observed (Figure 9a). The contact between the soil particles gradually transformed from point contact to surface contact, at which point the contact area was large and voids were filled effectively. Figure 9b reveals that the surfaces of the soil particles were covered by a mass of flocculent colloid. It filled the void, improved the angular surface, and enhanced the contact and connection. Finally, the strength of the solidified soil may have improved because of the relatively dense microstructure.



Figure 9. Microscopy image of solidified soil with slag and quicklime. (a) 100 µm scale; (b) 10 µm scale.

The X-ray powder diffractogram is shown in Figure 10. Combining the EDS and XRD analyses, it can be demonstrated that the main crystalline phase substances were quartz (SiO₂), albite (Na₂O·Al₂O₃·6SiO₂), anorthite (CaO·Al₂O₃·2SiO₂), CSH (CaO·SiO₂·H₂O), and CAH (CaO·Al₂O₃·H₂O). Quartz and albite were crystalline minerals that pre-existed in the dredger soil, and anorthite, CSH, and CAH were new reaction products. The reaction mechanism can be explained as follows: Ca(OH)₂ from CaO hydrolysis increased the pH value of the sample. Next, SiO₂ and Al₂O₃ were activated, which resulted in the formation of CSH and CAH colloids. The colloids filled the voids between the saline soil grains and then wrapped the grains to form a spatial network structure. As a result, the density and strength of the solidified soil improved significantly. The conclusion can be validated effectively by the results of the unconfined compression tests described in Section 3.2.1: the maximum 7 day and 28 day compressive strength reached 890 kPa and 2015 kPa, respectively, with 1% quicklime.



Figure 10. X-ray powder diffractogram of solidified soil with slag and quicklime.

4.2.5. Solidified Soil with Slag and Composite Additives

Figure 11a presents the microscopy image of solidified soil with slag and composite additives. It is evident that a compact overall structure was obtained. Moreover, few voids were observed. The soil surface was flat and covered with a layer of colloidal material. Figure 11b reveals that the flocculent colloid on the surface of soil grain filled the voids and wrapped the grains to form an overall structure. In addition, a significant amount of colloid formed continually and connected to constitute a spatial network structure, which may have contributed to a substantial increase in the strength of the solidified soil.



Figure 11. Microscopy image of solidified soil with slag and composite additives. (**a**) 100 μ m scale; (**b**) 10 μ m scale.

The X-ray powder diffractogram is shown in Figure 12. Combining the EDS and XRD analyses, it can be demonstrated that the main crystalline phase substances were quartz (SiO₂), albite (Na₂O·Al₂O₃·6SiO₂), AFt (3CaO·Al₂O₃·3CaSO₄·32H₂O), CSH (CaO·SiO₂·H₂O), and calcium aluminate chloride sulphate hydrate (3CaO·Al₂O₃·(0.5CaCl₂·0.5CaSO₄)·12H₂O). According to the above analysis with a single additive, AFt and calcium aluminate chloride sulphate hydrate were the new reaction products in the solidified soil with slag and composite additives. In particular, the Cl⁻ in the calcium aluminate chloride sulphate hydrate, which was derived neither from the slag nor from the three additives, indicated that the composite slag solidifying agent had the capacity to desalinate the dredger fill.



Figure 12. X-ray powder diffractogram of solidified soil with slag and composite additives.

5. Mechanism Analysis of Composite Slag Solidifying Agent

Based on the results of the microstructure investigation, it can be inferred that the analysis of the mechanism of a composite slag solidifying agent is essentially the clarification of the process of formation of CSH, AFt, and calcium aluminate chloride sulphate hydrate.

1. CSH

In the solidified soil, the source of CSH is the hydration of composite slag solidifying agent and the reaction of SiO_2 .

Based on the XRD results of unsolidified soil, it can be stated that SiO_2 was a main component in the dredger fill. In addition, the slag was essentially composed of SiO_2 , Al_2O_3 , CaO, and other oxides. NaOH and Ca(OH)₂ from sodium silicate and quicklime hydrolysis increased the pH value of the sample. Next, SiO_2 and other oxides were activated. Finally, CSH was obtained. The reactions are expressed as:

$$CaO + H_2O \rightarrow Ca(OH)_2$$
 (2a)

$$Na_2O \cdot SiO_2 + H_2O \rightarrow 2NaOH + SiO_2$$
 (2b)

$$SiO_2 + Ca(OH)_2 + H_2O \rightarrow CaO \cdot SiO_2 \cdot H_2O(CSH)$$
(2c)

2. AFt

In the solidified soil, AFt ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) was formed by the transformation of CAH. As introduced in Section 4.2.4, CAH was obtained in the solidified soil with slag and quicklime. The formation of the CAH was similar to that of CSH: Al_2O_3 was activated in an alkaline environment and combined with Ca(OH)₂ to form CAH colloids. The reactions are expressed as follows:

$$CaO + H_2O \rightarrow Ca(OH)_2$$
 (3a)

$$Al_2O_3 + Ca(OH)_2 + H_2O \rightarrow CaO \cdot Al_2O_3 \cdot H_2O$$
 (3b)

Next, AFt is formed by the combination of CAH and sulphate ion, which is obtained from gypsum powder:

$$CaO \cdot Al_2O_3 \cdot H_2O + CaSO_4 + H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$$
(3c)

3. Calcium aluminate chloride sulphate hydrate

Calcium aluminate chloride sulphate hydrate formed from the interaction between the composite slag solidifying agent and the soluble salt in the saline dredger fill. As presented above, a certain amount of CAH combined with sulphate ions in the gypsum powder to form AFt. Part of the remaining CAH reacted with Cl⁻ in the saline soil to form Friedel's salt (Fs: $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$). Next, the sulphate ions from the gypsum powder continuously replaced part of the chloride ions in Friedel's salt in the sulphate ion-enriched environment to eventually yield calcium aluminate chloride sulphate hydrate. The reactions are expressed as follows:

$$CaO \cdot Al_2O_3 \cdot H_2O + NaCl \rightarrow 3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O + NaOH$$
(4a)

 $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O + CaSO_4 \cdot 2H_2O \rightarrow CaCl_2 + 3CaO \cdot Al_2O_3 \cdot (0.5CaCl_2 \cdot 0.5CaSO_4) \cdot 12H_2O$ (4b)

The NaOH generated during the reaction, which provided an alkaline environment, further promoted the hydration of the slag powder and maintained the reactions. Therefore, soluble salts (such as Cl⁻) in saline dredger fill can be reduced effectively and, in turn, the solidified soil can exhibit good road performance.

To summarize, the mechanism of composite slag solidifying agent for saline dredger fill is essentially the formation of CSH, AFt, and calcium aluminate chloride sulphate hydrate. CSH is a colloid, which has a good gelling property. It can fill voids in soil, thereby increasing the bonding force between grains, and cover the surface of grains to produce an overall structure. AFt is a needle-bar crystal, which can fill voids to improve the compactness of soil. The intersecting needle-bar crystal structures combine with CSH to obtain a spatial network structure, which plays a good supporting role in soil. It causes voids to be thinner or even disappear. The effect of AFt formation can compensate for the shortage of CSH and further improve the strength of solidified soil. In addition, CAH can combine with SO_4^{2-} and Cl^- in the soil to form calcium aluminate chloride sulphate hydrate, which can effectively reduce the content of soluble salts in saline dredger fill and substantially improve the engineering characteristics of solidified soil.

6. Conclusions

The solidification of Caofeidian dredger fill is difficult because of salinization, as well as environmental and economic factors. In this study, the composite slag solidifying agent proposed was experimentally detected by an unconfined compression test and microanalysis. Based on the results, the following conclusions can be drawn:

- 1. The composite slag solidifying agent can substantially improve the unconfined compressive strength of Caofeidian saline dredger fill. The additive quicklime contributes the most to this improvement. The optimal proportion is obtained as 10% slag + 1.0% quicklime + 0.8% sodium silicate + 1.5% gypsum powder.
- 2. The microanalysis illustrates that a compact overall structure was obtained and few voids were observed in the solidified soil with the composite slag solidifying agent. This is an apparent improvement in the microstructure compared with that of unsolidified soil or solidified soil with slag and a single additive (quicklime, sodium silicate, or gypsum powder).
- 3. The mechanism of composite slag solidifying agent for saline dredger fill is essentially the formation of CSH, AFt, and calcium aluminate chloride sulphate hydrate. First, the CSH colloid formed by slag hydrolysis improves the compactness of the soil. Second, AFt (formed by the combination of CAH and SO_4^{2-}) can further strengthen the microstructure of the solidified soil. Finally, CAH can combine with SO_4^{2-} and Cl^- in the soil to form calcium aluminate chloride sulphate hydrate, which can effectively reduce the content of soluble salts in saline dredger fill and substantially improve the engineering characteristics of solidified soil.

These observations are helpful for understanding the solidification mechanism of saline dredger fill and can provide a theoretical basis for future solidification projects in coastal saline dredger fill areas. In a future study, these observations could be verified with different dredger soils from other locations and field tests.

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Appendix A



Figure A1. EDS results of unsolidified soil. (a) Representative region; (b) EDS diffractogram.

Element	С	0	Na	Mg	Al	Si	C1	К	Ca	Fe	Zr
Mass percent (%)	11.03	48.84	4.68	0.86	6.52	15.87	2.69	1.34	3.99	2.64	1.55
Atomic percent (%)	17.36	57.71	3.85	0.66	4.56	10.68	1.43	0.65	1.88	0.89	0.32



Figure A2. EDS results of solidified soil with slag and gypsum powder. (a) Representative region; (b) EDS diffractogram.

 Table A2. EDS element determination results of solidified soil with slag and gypsum powder.

Element	С	0	Al	Si	S	Ca	Fe	Zr
Mass percent (%)	8.16	56.0	3.94	24.78	0.59	2.05	2.50	1.98
Atomic percent (%)	12.71	65.5	2.73	16.51	0.35	0.96	0.84	0.41



Figure A3. EDS results of solidified soil with slag and sodium silicate. (a) Representative region; (b) EDS diffractogram.

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Element	С	0	Na	Mg	Al	Si	S	C1	К	Ca	Fe	Zr
Mass percent (%)	13.97	48.18	1.95	1.21	7.27	14.99	0.32	0.50	3.21	3.98	2.36	2.05
Atomic percent (%)	21.61	55.94	1.58	0.93	5.00	9.91	0.18	0.26	1.53	1.85	0.78	0.42



Figure A4. EDS results of solidified soil with slag and quicklime. (**a**) Representative region; (**b**) EDS diffractogram.

Table A4. EDS element determination results of solidified soil with slag and quicklime.

Element	С	0	Na	Mg	Al	Si	Cl	K	Ca	Fe	Zr
Mass percent (%)	0.60	55.56	1.24	1.71	5.99	21.54	1.50	1.81	5.19	3.85	1.68
Atomic percent (%)	0.26	71.61	1.11	1.45	4.57	15.82	0.87	0.95	2.67	1.42	0.38



Figure A5. EDS results of solidified soil with slag and composite additives. (**a**) Representative region; (**b**) EDS diffractogram.

Table A5. EDS element determination results of solidified soil with slag and composite additives.

Element	С	0	Na	Mg	Al	Si	S	Cl	К	Ca	Fe	Zr
Mass percent (%)	15.25	52.01	1.37	1.52	4.26	14.13	1.34	0.80	0.90	5.12	1.71	1.59
Atomic percent (%)	22.81	58.40	1.07	1.12	2.83	9.04	0.75	0.41	0.41	2.29	0.55	0.31

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