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Laboratory Study on the Use of Urease-Induced Calcium Carbonate Precipitation for Stabilization of Coal Fly Ash

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Abstract: Coal fly ash (FA) dust negatively impacts human health and the environment. This study aimed to prevent wind erosion through the technology of enzyme-induced carbonate precipitation (EICP) to improve the surface stability of FA. In order to investigate the influence of urease activity, salt solution ratio, and polyacrylamide (PAM) concentration on the EICP process, unconfined compressive strength (UCS) test, sieving test, and wind tunnel test was carried out in the laboratory. Scanning electron microscopy (SEM) was also used to analyze the microscopic crystal morphology characteristics of mineralized products. The results showed that the wind erosion rate of the samples treated with EICP reduced significantly (the minimum wind erosion rate is $1.986 \text{ mg}/(\text{m}^2 \cdot \text{min})$) due to the crystal bridge function of CaCO_3 , while the UCS of these samples increased clearly. Appropriately increasing urease activity in the treatment solution contributed to the increased CaCO_3 content and microscopic size. Excess urea concentration had a certain inhibitory effect on urease activity. The addition of PAM provided more nucleation sites for the EICP process and improved the strength of the cementation. These findings suggested that the EICP-PAM was a promising technique for the protection of FA sites from wind erosion.

Keywords: enzyme-induced carbonate precipitation; coal fly ash; unconfined compressive strength; wind erosion; scanning electron microscopy



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1. Introduction

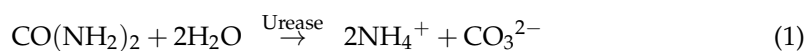
Mineral resources have been the basic guarantee of human social life; however, the development of mineral resources has brought many environmental problems, such as mine waste emission and heavy metal pollution, which have a wide impact and serious consequences. As the main energy source for most countries in the world, coal production is expected to increase to 4032 million tons in 2035 [1]. Coal-fired power has been a major form of coal utilization, which generates a large amount of coal fly ash (FA) [2]. However, the utilization rate of FA was very minimal compared to its production rate, and more than half of the FA was piled up in the vicinity of thermal power plants [1]. FA contains mercury, arsenic, lead, cadmium, chromium, and other heavy metals [3]. High-speed wind can easily detach the exposed surficial FA and suspend them in the air, causing serious impacts on the environment and human health [4]. FA has been considered a main industrial pollutant [5]. Therefore, it is imperative to mitigate the wind erosion of FA sites.

A wide variety of FA stabilizing methods have been used to reduce wind erosion of FA sites [4]: ① Water sealing method, which is fast but needs to be carried out regularly, is especially not suitable for arid areas; ② Imported soil cover method, which is thorough, but requires a large quantity and comes at a high cost, the application of imported soil to control FA dust does not have optimistic prospects under the current national land resources protection policy; ③ Ash field planting method, which used trees to suppress the generation of dust and improve the local environment. Unfortunately, the effect of the ash field planting method is poor and easily affected by seasonal climate changes. Therefore, this kind of method is only suited for a completely abandoned ash deposit site.

④ Surface-cured dust control, which is a new method that combines physical and chemical methods to control dust for ash sites, spraying active materials which will react with the loose particles on the surface of FA sites to produce a gummy substance and form a solid layer with a certain strength to prevent FA sites from wind erosion [6]. The outstanding advantage of this method is the low-cost and simple construction process used both in service and end-of-service FA sites. Therefore, surface-cured dust control is a promising dust control technique.

In the process of seeking new active curing materials, it was found that Microbially Induced Carbonate Precipitation (MICP) might be a promising environmental technique [7,8] for solidifying loose particles (such as sand and soil). MICP improved the stiffness, strength [9,10], erosion resistance [11,12], and impermeability [13] of loose bodies based on the cementation of CaCO_3 crystals between loose particles, the technique of which also has the advantages of easy synthesis [14], etc. Furthermore, MICP has shown promising potential for the suppression of fugitive dust [15,16]. However, the use of bacteria for MICP requires a series of preparatory steps, such as bacterial culture and preservation, which are complex [17] and costly [18]. Moreover, there was a lack of effective monitoring of the possible effects of introducing foreign bacteria into the soil on indigenous microorganisms.

Urease plays an important role in the reaction mechanism of MICP, which is widely found in nature (e.g., soybeans, raised cut beans, mulberry leaves, etc.). As a biological enzyme, urease has a high production efficiency over a wide temperature (ranging from 10 to 70 °C) [19]. A large number of research projects have shown that the effects of using urease only and using active bacteria to catalyze urea hydrolysis were similar [20]. Therefore, Enzyme Induced Carbonate Precipitation (EICP) is used as a new technique to cure loose particles. The products of EICP include ammonium (NH_4^+) and carbonate (CO_3^{2-}), which are produced by the enzymatic hydrolysis of urea in the first step (Equation (1)). Subsequently, the precipitation of CaCO_3 crystals formed by the connection between CO_3^{2-} and soluble calcium ions (Ca^{2+}) in an alkaline environment (Equation (2)) [21].



The technique of EICP has attracted lots of attention from scholars because of its energy-saving, eco-friendly, and economic efficiency [21]. For example, the surface strength of desert sand cured by EICP increased nearly 20 times higher compared to the untreated sample [19].

The surface of soil particles and sand grains is rough and carries a large number of organics that provide a large number of nucleation sites for CaCO_3 crystals, the microorganisms in the MICP process are also used as nucleation sites for CaCO_3 precipitation [22]. Polyacrylamide (PAM) is considered to be added to the EICP solution because the surfaces of most FA particles are smooth. PAM has good characteristics of thermal stability and is eco-friendly [23]. A chain-like structure is formed when PAM is dissolved in water, which can adsorb, wrap, and bond loose particles [24].

Some previous experiments using EICP and PAM, respectively, to cure sand have been presented, but few of them combined these two materials for curing [19]. In particular, the research on the solidification of FA with this bio-technique remains significantly understudied. Therefore, the presented herein approaches FA as the primary focus of the study; additionally, this study includes:

- (1) Study the effects of urease activity, salt solution ratio, and PAM concentration on the stabilization of FA.
- (2) Qualitative and quantitative research to evaluate each influencing factor from the perspectives of unconfined compressive strength (UCS), wind erosion rate, and agglomerated particle size to reveal the variation law and lay the foundation for the optimization of FA curing techniques.

- (3) Investigate the mechanism of FA samples cured with EICP techniques by observing the microstructure through scanning electron microscopy (SEM) and analyzing material compositions through Energy Dispersive X-ray Spectroscopy (EDX).
- (4) Determine the optimum ratio of EICP curing agents.

2. Materials and Methods

2.1. Material

2.1.1. FA

The FA for the experiments was collected from the pithead power plants in the Dananhu Area, Hami, Xinjiang. The coal seams are mainly exposed in the southeastern edge of the Tuha Basin, a typical terrestrial coal-bearing basin developed in the Xishanyao Formation. The coal seams formed in a fluvial-deltaic sedimentary environment. The results of XRD analysis show that the main mineral composition of FA is quartz, with a small amount of mullite and hematite and a very small amount of calcite (Figure S1). The main chemical components (Table S2) in FA are SiO_2 and Al_2O_3 , with a small amount of Fe_2O_3 and CaO . The results of trace element analysis (Table S2) indicate that the contents of some heavy metals in FA are significantly higher than that in Shenhua Power Plant, which is located in the Wucuiwan mining area, eastern Junggar coalfield [1]. The particle size of FA was concentrated in 0.005–0.2 mm (Figure S2).

2.1.2. PAM

The PAM used in the test was anionic polyacrylamide (analytically pure, AR), which was a white pulverized particle with a relative molecular mass of 12 million, produced by Tianjin Zhiyuan Chemical Reagent Co., Ltd. (Tianjing, China)

2.1.3. Urease

The urease used in the test was produced by Nanjing Biological Products Co., Ltd. (Nanjing, China). Urease is a kind of protein, and the urease activity (define: one unit causes the formation of two micromoles of ammonia per minute at pH 8.0 at 37 °C) was about 276 u/mg at 37 °C. The urease was diluted with deionized water to a dilute solution of 13.8 u/mL.

2.1.4. Other Materials

The exogenous calcium used in the test was anhydrous CaCl_2 (AR), a kind of white powder with a relative molecular mass of 110.98; the urea (AR) was a white crystalline powder with a relative molecular mass of 60.06. Both materials were produced by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Anhydrous CaCl_2 and urea were dissolved into 0.3 mol/L CaCl_2 solution and 0.3–2 mol/L $\text{CH}_4\text{N}_2\text{O}$ solution with deionized water.

2.2. Sample Preparation

2.2.1. Sample

The virgin FA was air-dried and then passed through a 0.5 mm standard sieve. To meet different test requirements, samples were divided into a large sample and a small sample. The large samples were mainly used for wind erosion tests, etc., and the small samples were mainly used for mechanical tests, etc. The following steps were carried out to make the dry density of each group of samples approximately the same: for large samples, about 100 g of FA was loaded into the sample plate with the size of 17.5 cm × 11.3 cm × 2.2 cm (length × width × height), and then tapped for 10 times along the circumference of the plate; for small samples, about 100 g of FA was loaded into the sample cup with the bottom diameter of 3.5 cm, and then the cup was tapped for 10 times.

2.2.2. Solution

The treatment solution was divided into a blank control group, an EICPa group, an EICPb group, and an EICP-PAM group. The blank control group included the virgin FA sample and the sample treated with deionized water). The EICPa group was used to investigate the effect of changes in urease activity on the curing effect when the salt solution concentration remained constant (i.e., the concentration of CaCl_2 was 0.3 mol/L; the concentration of urea was 1 mol/L). The EICPb group was used to evaluate the effect of changes in the salt solution concentration (the concentration of CaCl_2 always remained at 0.3 mol/L) on the curing effect when urease activity remained constant (460 u). The EICP-PAM group included the control sample treated with PAM only, which mainly explored the effect of the changes in urease activity on the curing effect of EICP based on a certain PAM concentration (0.6 g/L). The detailed composition of different treatment solutions is shown in Table 1.

Table 1. Composition of different treatment solutions.

No.	Composition	Urea (mol/L)	CaCl_2 (mol/L)	Urease (Activity: u)	PAM (g/L)
1	U	The blank control samples were treated with deionized water			
2	T-0-0-0-0				
3	T-1-0.3-4.6-0	1	0.3	4.6	0
4	T-1-0.3-46-0	1	0.3	46	0
5	T-1-0.3-92-0	1	0.3	92	0
6	T-1-0.3-138-0	1	0.3	138	0
7	T-1-0.3-460-0	1	0.3	460	0
8	T-1-0.3-920-0	1	0.3	920	0
9	T-0-0-460-0	0	0	460	0
10	T-1-0-460-0	1	0	460	0
11	T-0.3-0.3-460-0	0.3	0.3	460	0
12	T-0.6-0.3-460-0	0.6	0.3	460	0
13	T-1.5-0.3-460-0	1.5	0.3	460	0
14	T-2-0.3-460-0	2	0.3	460	0
15	T-0-0-0-0.6	0	0	0	0.6
16	T-1-0.3-0-0.6	1	0.3	0	0.6
17	T-1-0.3-4.6-0.6	1	0.3	4.6	0.6
18	T-1-0.3-46-0.6	1	0.3	46	0.6
19	T-1-0.3-92-0.6	1	0.3	92	0.6
20	T-1-0.3-138-0.6	1	0.3	138	0.6
21	T-1-0.3-460-0.6	1	0.3	460	0.6
22	T-1-0.3-920-0.6	1	0.3	920	0.6

Note: in the columns of “composition” of the table, the letter “U” indicates the untreated sample; “T” represents the treated sample, and the number means the amount of each chemical.

For large samples, the treatment solution (deionized water was used for the blank control) was sprayed evenly on the surface of the sample using the spray at a dosage of 0.45 L/m². For small samples, considering the liquid limit value of FA was 32% [4], every 10 g of FA was sprayed with the treatment solution of 3 mL (the same volume of deionized water was used for the blank control) to ensure the full contact between the treatment solution and FA. All types of samples were provided with 3–12 groups of parallel samples (the number of groups was adjusted according to the requirements of the test). The vertical distance from the nozzle of the spray to the surface of the specimen was 25 cm to prevent the impact of the water mist from damaging the flatness of the sample surface. In order to minimize the biochemical reaction process in the sprayer, the spray was completed in a short time.

2.2.3. Standard Maintenance

To make the cured reaction sufficient, all treated samples (including the blank control group) were cured at room temperature for 10 days (temperature: 28.4 °C; humidity: 49.4%) and dried in an oven (temperature: 60 °C; time: 12 h) before the test.

2.3. Methods

The UCS, Shaking and Sieving (see Methods in Supporting Information (SI) for details), Wind-tunnel test, Water-stability test, and Freeze-thaw test were carried out for the prepared samples to characterize their curing properties.

2.3.1. Water-Stability Test

The water-stability of the surface for cured FA was an important reference indicator to evaluate the final service life for the cured site [25]. The rainfall process was simulated by spraying deionized water on the top of samples, about 10 g water for each large sample and 15 g water for each small sample, and then these samples were dried in an oven at 60 °C for 24 h. This process was one wet-dry cycle, and so on for up to three times.

2.3.2. Freeze-Thaw Test

The cured FA must be able to withstand extreme temperatures in nature. Freeze-thaw cycles usually cause perturbations to FA crusts and result in a reduction in surface strength and wind erosion resistance [26]. Deionized water was sprayed with about 5 g for each large sample and 10 g for each small sample, and then they were immediately placed in a freezer at about −20 °C for 12 h and then taken out and dried for 12 h (at a temperature of 60 °C), this process was for one freeze-thaw cycle, and so on for three times.

2.3.3. Other Tests

The particle size of FA was tested by Laser particle size analyzer HELOS (H2566) and QUIXEL, and the result of which was analyzed by PAQXOS software (Neopatek, Germany). The microstructure of the cured crust for the FA was observed by ZEISS Gemini 300, and the Spectrum model was Smartedx. The Methods of X-ray diffraction (XRD) analysis and Chemical component analysis were introduced in SI for details.

2.4. Statistical Analysis

All the experiments were conducted in three replicates to ensure the accuracy of the experimental data. The final data were presented as means ± standard deviation (SD) in the tables (Tables S2 and S4). The analysis of variance (ANOVA) at the 0.05 level was performed to determine the significant difference among treatments performed by SPSS v.25.0 for Windows (IBM Inc., Chicago, IL, USA). The other statistical analysis was also conducted by SPSS v.25.0 for Windows. All figures were plotted and compared using Origin 9.8 (Origin Lab Corp., Northampton, MA, USA).

3. Results and Discussion

3.1. UCS Analysis

The UCS of the control sample (T-0-0-0-0), which was treated with deionized water, was only 41.3 kPa (Figure 1, Table S2). The CaO contained in the FA reacted with water to generate Ca (OH)₂, which would react with the CO₂ dissolved in the water to produce a limited amount of CaCO₃ deposition, explaining the fact that the UCS of this group sample increased slightly after the wet-dry cycles. The UCS of the sample (T-0-0-460-0) with urease added to it was slightly higher (46.9 kPa) than that of the control sample, indicating that the enzyme, which was a kind of protein, has a slight cementing effect, and this also suggests that no substance could be hydrolyzed by urease in FA itself. The USC of the sample with added urea (T-1-0-460-0) increased significantly (189.0 kPa), indicating that a large amount of CO₃^{2−} ions were generated due to the hydrolysis of urea by urease in the treatment solution, which reacted with calcium in the FA samples to produce CaCO₃ deposition,

thus resulting in the goal of cementing the FA. The UCS of the sample treated with both urea and exogenous calcium (CaCl_2) (T-1-0.3-460-0) was significantly increased (694.6 kPa), which was 17 times higher than that of the control sample, reflecting the involvement of exogenous calcium in the production of CaCO_3 . The UCS of the sample treated with PAM solution (T-1-0-0-0.6) was 367.7 kPa, which reflected a strong cementing effect of the macromolecular polymer on the particles of the FA [4].

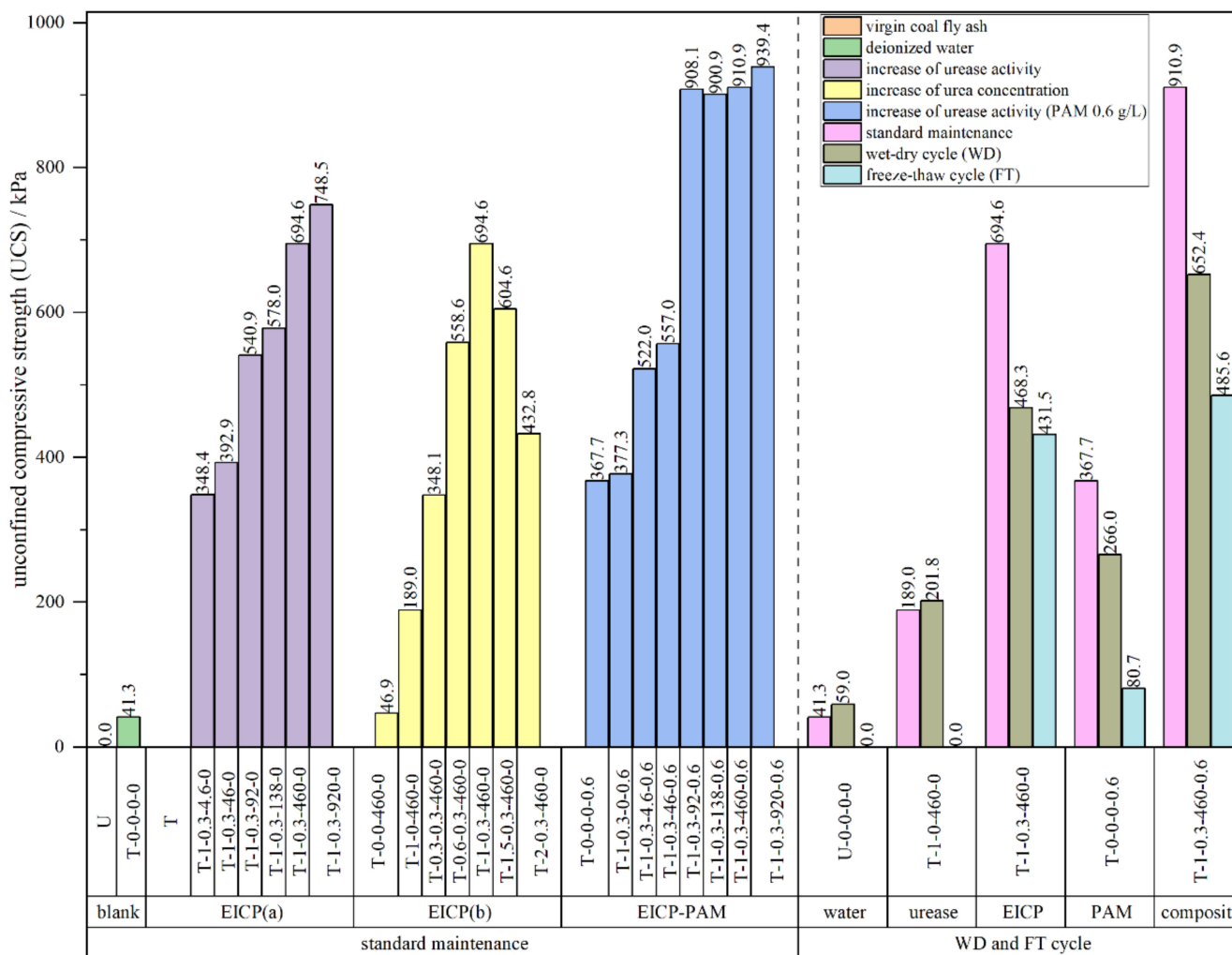


Figure 1. UCS of samples cured with different treatment solutions.

The UCS of the samples increased dramatically with the increase in urease activity (purple column in Figure 1) when the concentrations of urea and CaCl_2 were constant (1 mol/L; 0.3 mol/L, respectively), and the peak strength was 748.5 kPa (T-1-0.3-920-0), indicating that the highly active enzyme promoted a large amount of CaCO_3 deposition in the process of EICP. The CaCO_3 increased the compressive strength and the bonding force between FA particles, the result of which was similar to the previous study reported by Meng et al. [27]. On this basis above, when the same concentration of PAM solution (0.6 g/L) was added, the UCS of the specimen increased significantly. The urease activity increased from 0 u to 92 u, and after that, little obvious improvement of the sample strength could be further observed along with the increase in urease activity (blue column in Figure 1). It has been reported that the higher the activity of urease, the shorter the reaction time of EICP. Additionally, the addition of PAM increased nucleation sites of CaCO_3 , leading to a rapid mineralization reaction and a large amount of CaCO_3 being randomly generated. This results in filling up the pore spaces between FA particles and easily blocking the permeability pathway of the treatment solution [21], therefore, resulting in a non-uniform

mineralization reaction in the specimen. On the other hand, the limited area where bond-making (i.e., possible binding points between particles) [28,29] has already been filled. Previous studies have shown that CaCO_3 crystals in the bond-making areas were likely to provide strength to the cementing crystals [27], and the limited pore space in the sample has been filled by the CaCO_3 crystals that formed early, so the secondary CaCO_3 crystals make little contribution to cementation in this area. Therefore, the increase in the UCS in these samples was not obvious.

On the basis of a specific concentration of exogenous calcium (i.e., CaCl_2 : 0.3 mol/L) and urease activity (460 u), the UCS of the samples increased and then decreased along with the increase in urea (yellow column in Figure 1), and the maximum value (694.6 kPa) appeared when the concentration of urea was 1 mol/L. Studies have shown that a moderate concentration of urea has the effect of promoting calcite cementation, while a higher concentration of urea would reduce the precipitation efficiency of CaCO_3 [30].

The samples treated with deionized water (T-0-0-0-0) and those treated with both urea and urease (T-1-0-460-0) had lower UCS after wet-dry cycles, and they had poor frost resistance, indicating that the generation of CaCO_3 deposition was very limited when only dependent on endogenous calcium. The cementation of this type of CaCO_3 crystal contributed little to the structural strength of the samples. Compared with the standard curing sample (i.e., without wet-dry and freeze-thaw cycles), the water stability strength and frost resistance strength of the EICP treated samples (T-1-0.3-460-0) were reduced by 32.58% and 37.88% respectively. Previous studies have shown that loose particles treated by MICP had better resistance to freeze-thaw cycles [31]. The strength loss of the samples might be caused by ① the unreacted urea and CaCl_2 may have been hydrolyzed and migrated due to the repeated cycles of wet-dry and freeze-thaw, resulting in partial strength failure caused by precipitation of salt; ② a few of the CaCO_3 precipitates of smaller size (range in microns) were only weakly cemented to FA particles, and the loose particles cemented by this kind of CaCO_3 crystals acted as a cementing agent were destroyed easily and suspended rapidly during wet-dry and freeze-thaw cycles, resulting in a decrease in the strength of the samples [32]. Compared to the standard cured samples, the water stability strength and frost resistance strength of the PAM-treated samples (T-0-0-0-0.6) decreased by 27.66% and 78.05%, respectively, probably caused by the degradation of the PAM hydrogel bonds formed in the pores between the FA particles due to repeated freeze-thaw cycles [33]. For the samples treated by the EICP-PAM, in addition to the cementing effect of salt, protein, and polymer in the treatment solution, the CaCO_3 formed by EICP was deposited between the pores of FA, which made the curing effect more significant (i.e., the strength of water stability and frost resistance improved clearly).

The comprehensive analysis concluded that the initial concentration of urea and Ca^{2+} ions and the initial activity of urease in the treatment solution influenced the rate of mineralization and reactants utilization directly. The higher active urease could catalyze more urea hydrolysis to produce CO_3^{2-} ions which rapidly combined with Ca^{2+} ions. However, excessive concentration of urea would inhibit the mineralization reaction. The incorporation of PAM improved the brittle failure characteristics of cured FA.

3.2. Agglomerated Particle Size Analysis of the FA

The percentage of agglomerates (i.e., the particle size of the FA was equal to or more than 0.5 mm) in the total mass of the samples gradually increased after being treated with deionized water (T-0-0-0-0), urease (T-0-0-460-0), the mixture of urease and urea (T-1-0-460-0), PAM (T-0-0-0-0.6), EICP (T-1-0.3-460-0) and EICP-PAM (T-1-0.3-460-0.6) respectively, in the order of 0.21%, 0.24%, 0.35%, 0.54%, 1.54% and 21.01% (Figure 2a; Table S3).

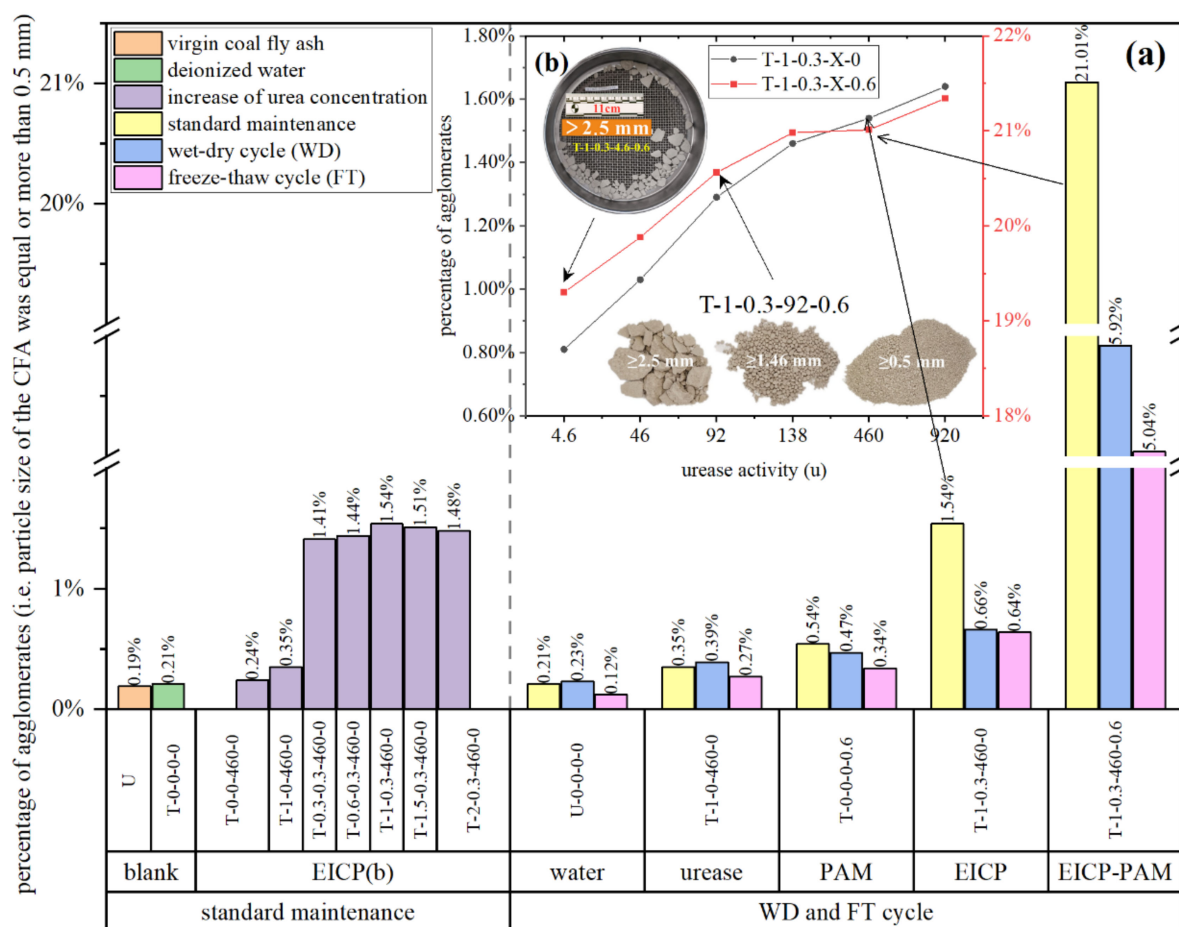


Figure 2. Percentage of agglomerates (i.e., the particle size of the FA was equal to or more than 0.5 mm) in the total mass of the sample after being cured with different treatment solutions. (a) Percentage of agglomerates of samples at different curing methods and concentrations of treatment solution; (b) effect of urease activity in the treatment solution on the size of agglomerated particles in cured FA.

Based on a certain concentration of the salt solution (urea: 1 mol/L; CaCl_2 : 0.3 mol/L), the agglomerates percentage of cured FA gradually increased with the increase in urease activity (black dots in Figure 2b), with a peak of 1.64%, indicating that CaCO_3 generated in the EICP process was filled the pores of FA and bonded FA particles together. After continuing to add 0.6 g/L PAM in the treatment solution, the agglomerates percentage of the samples increased significantly with the increase in urease activity (red square dots in Figure 2b), and the trend became stabilized when the urease activity was greater than 138 u, with a peak of 21.34%. The hydrolysis of urea created an alkaline microenvironment during the EICP process, which was more favorable for the adsorption of Ca^{2+} on the PAM surface [34], leading the precursor concentration of crystal to reach supersaturation, and then the CaCO_3 crystal was precipitated. Previous studies have shown that heterogeneous nucleation occurs when the solution system contains substances such as organic matter, which increase the nucleation rate [35]. CaCO_3 crystals grew and accumulated on the PAM adsorbed on the FA surface, building bridges between particles, forming wraps on the particle surface, and enhancing the cementation of the FA particles. Eventually, there formed a mesh-like three-dimensional structure by cross-winding and linking chain-like adsorbents (PAM) among the pores between the particles. Therefore, the particle size of the agglomerates and the stability of the FA samples increased significantly.

Based on a certain activity of urease (460 u) and concentration of exogenous calcium (CaCl_2 : 0.3 mol/L), the agglomerate particle size of the cured samples increased rapidly with the increase in urea concentration, with a peak (1.54%) at urea concentration of

1 mol/L and then showed a weak decreasing trend, which indicated that along with the increase in reactants in EICP process, there would be more CaCO_3 deposition generated, while the inhibitory effect on urease activity gradually became prominent when the urea concentration was too high.

Comparing the samples treated with deionized water, EICP (without exogenous calcium), PAM, EICP, and EICP-PAM in the condition of wet-dry and freeze-thaw cycles, the percentage of the agglomerated particles in the samples increased in order. It has been shown that soils dominated by large aggregates resisted freeze-thaw cycles better [36]. Therefore, based on the presence of agglomerated particles, the stability in water of FA cured by EICP-PAM (T-1-0.3-460-0.6) increased about 9 times and 13 times compared with the samples treated with EICP (T-1-0.3-460-0) and PAM (T-0-0-0-0.6) alone, respectively. The frost resistance increased about 8 times and 15 times compared with the samples treated with EICP and PAM alone, respectively, indicating that the technique of using EICP-PAM promoted the increase in cementation strength and effective particle size of FA.

3.3. Wind Erosion Resistance Analysis

The blank control sample without any treatment had the largest wind erosion rate, which was 39.567 $\text{mg}/(\text{m}^2 \cdot \text{min})$ at a wind speed of 10 m/s (Figure 3; Table S4, the direction of the arrow in the physical photo represented the wind direction); while the sample treated with EICP-PAM had the lowest wind erosion rate, which was only 1.455 $\text{mg}/(\text{m}^2 \cdot \text{min})$.

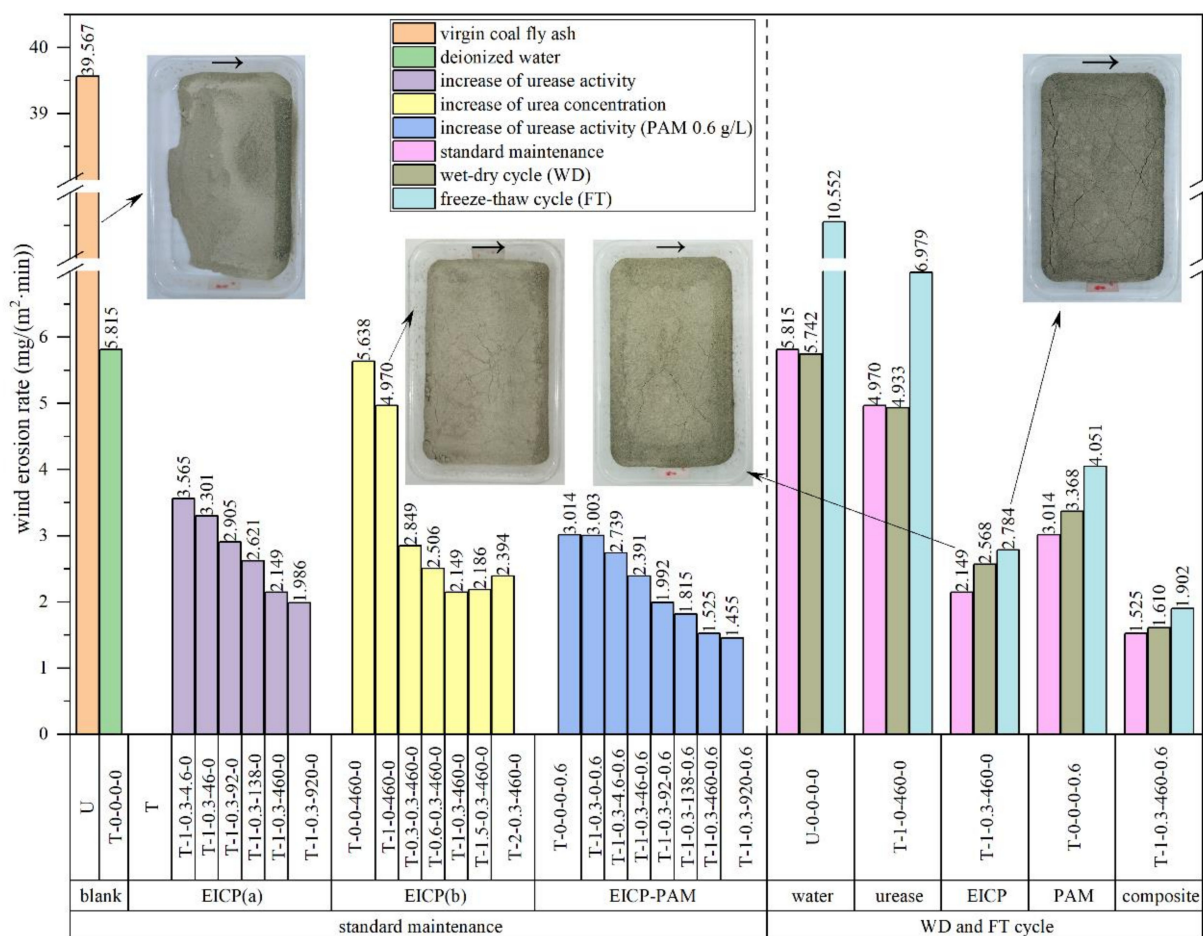


Figure 3. Wind erosion rate of FA samples untreated and treated with different means.

Based on a constant salt solution concentration (i.e., urea 1 mol/L; CaCl_2 : 0.3 mol/L), the mass loss of FA samples gradually decreased with the increase in urease activity (purple column of Figure 3) under a wind speed of 10 m/s. The minimum wind erosion rate was

1.986 mg/(m²·min) when the urease activity increased to 920 u, suggesting that higher urease activity was an important factor in the formation of crust and reduction in wind erosion. A similar conclusion was drawn by Naeimi and Chu [6] in a laboratory test using MICP-cured sandy soil. When added 0.6 g/L PAM in the EICP treatment solution, the wind erosion rate of the samples decreased along with the increase in urease activity (blue column of Figure 3), and the minimum wind erosion rate was 1.455 mg/(m²·min). PAM increased the viscosity of the treatment solution, which in turn reduced the separation of particles [19].

The mass loss of the sample was observed after being blown at the wind speed of 10 m/s (yellow column in Figure 3) when the urea concentration was adjusted only in the EICP solution. When the urea concentration increased to 1 mol/L, the mass loss of the sample was minimal (2.149 mg/(m²·min)). After that, the mass loss increased slowly, reflecting the excess salt had a certain inhibitory effect on the enzyme activity.

All of the FA samples cured with EICP, PAM, and EICP-PAM treatment solutions showed a slight increase in wind erosion rates after undergoing the wet-dry and freeze-thaw cycle tests compared with the standardly maintained samples (Figure 3). The deformation of the soil skeleton and destruction of the pore structure was formed due to wet-dry and freeze-thaw cycles, which in turn led to the formation of cracks where particles easily escape and then resulted in wind erosion [37]. In particular, the freeze-thaw cycle weakened the cementation between FA particles. When the pore water between FA particles condensed into ice, causing the expansion, extension compressed the surrounding particles. Later, when the ice melted into the water, the framework between FA particles could not be restored completely. Therefore, with the increase in freeze-thaw cycles, the UCS of the samples treated with deionized water decreased from 41.3 kPa to 0, and the wind erosion rate increased from 5.815 mg/(m²·min) to 10.552 mg/(m²·min). However, the mass change of the samples treated with EICP-PAM was not significant before and after freeze-thaw cycles, which was mainly caused by the CaCO₃ crystals generated by EICP acted as the connection point and provided a binding force for FA to resist freeze-thaw cycles [38]. In addition, an abundance of amide groups on the PAM molecular chain could be hydrolyzed and transformed into polymers containing carboxyl groups, which attached to the surface of FA particles through van der Waals forces, attractive electrostatic forces, and hydrogen bonds, forming an incompletely continuous and dense spatial skeleton network system structure between FA particles. This additional flexible cementation inhibited the separation of particles and enhanced the additional resistance to freeze-thaw weathering. Naeimi and Chu [6] showed a similar experimental result.

3.4. Correlation Analysis of Cured Properties for FA Samples

There was a strong relationship between the wind erosion rate, UCS, and agglomerate particle size of FA samples after being treated with EICP and EICP-PAM, respectively (Figure 4).

The strength and the agglomerate particle size of the FA sample determined the wind erosion rate [27]. There was a linear relationship between the wind erosion rate and the UCS (Figure 4a). With the increase in the UCS, the wind erosion rate of the samples decreased (i.e., the resistance strength of wind erosion increased), and the agglomerate particle size and the wind erosion rate of the samples were negatively correlated (Figure 4b), but positively correlated with the UCS (Figure 4c), and all of the absolute values of the slope for the samples treated by EICP were larger, indicating that the EICP technique was very effective in reducing the wind erosion rate and increasing the UCS of the samples. Correlation analysis showed that with the optimization of the curing scheme (i.e., treatment solution composition changed from deionized water to EICP and EICP-PAM), the structural stability and UCS of FA increased, which achieved a good windproof ash consolidation effect.

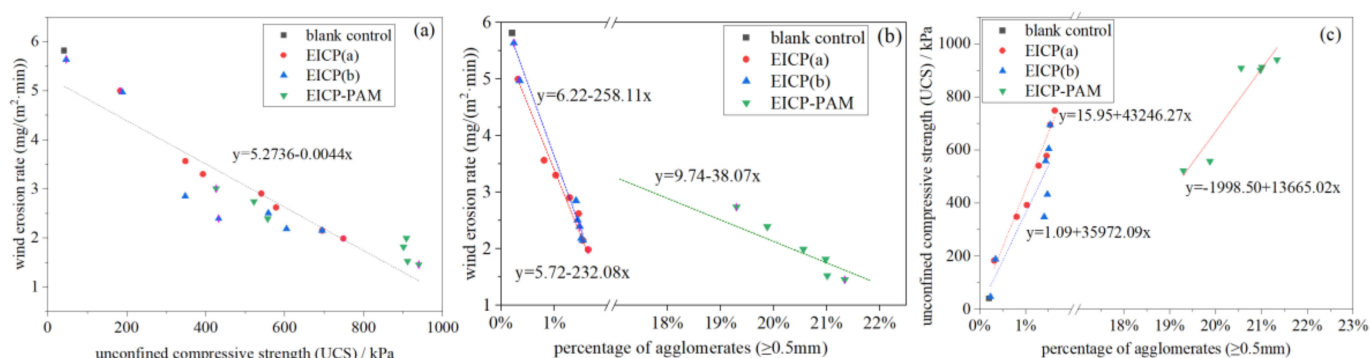


Figure 4. Correlation analysis of FA samples treated with EICP and EICP-PAM, respectively. (a) Relationship between UCS and wind erosion rate; (b) relationship between agglomerates and wind erosion rate; (c) relationship between agglomerates and UCS.

3.5. SEM Imaging and EDX Analysis

To further investigate the mechanism of EICP and EICP-PAM in cured FA, SEM was conducted after standard maintenance of these specimens to observe the microstructural differences within the FA crusts formed by mineralization. It could be found that the type and concentration of the chemical in the treatment solution have important effects on the size and density of the mineralized crystal structure from Figure 5, which showed the microscopic images of FA cured by deionized water (Figure 5a), EICP (Figure 5b), PAM (Figure 5c), and EICP-PAM (Figure 5d–f), respectively.

The boundaries of FA particles were clear in the control group samples treated with deionized water (Figure 5a). The pores between particles were large (Figure 5a), a few CaCO_3 crystal particles with particle sizes less than $0.5 \mu\text{m}$ formed by CO_2 in the air as an inorganic carbon source [39], and endogenous calcium scattered on the smooth surface of some FA particles. The samples treated by EICP generated more CaCO_3 crystals (Figure 5b), part of which was used to fill the pores and increase the compactness of the space structure for the FA samples; and part of which acted as bridges to cement FA particles [40] and increased the cohesive force of the samples [41]. However, the CaCO_3 crystals were still relatively sparse, and a little of large pores between FA particles also existed. Rough gelatinous materials were distributed on the surface of FA in samples treated with PAM (Figure 5c). The PAM, which bonded FA pellets with pellets. For the samples treated with EICP-PAM, in addition to the “bridge function,” a “rough film” was formed due to some FA particles being wrapped by PAM and CaCO_3 crystals (Figure 5e), leading to the boundary of FA particles becoming blurred.

EDX was performed to analyze the mineralogical composition of samples in the SEM. Figure 6a shows the elemental spectra obtained from the energy spectral analysis of the sample treated by EICP, each wave peak of the energy spectra indicated the relative concentration of the elements.

The main chemical composition of FA included O, Si, Al, and small amounts of Fe, Ca, and C (Table S5). Compared with the virgin FA, the samples treated with EICP and EICP-PAM showed a significant increase in C and the appearance of N. It also could be found that the elements of Ca were mainly distributed on the surface of FA particles and the spherical material in the pores between the particles (Figure 6b). The spherical material was probably CaCO_3 deposition due to the overlapping of Ca and C in Figure 6b.

Crystal morphology was often used as one of the important symbols to distinguish mineral types [42], the differences of which affect the effectiveness of CaCO_3 crystal in bio-solidification eventually [43,44]. There were usually three different amorphous forms of calcium carbonate, namely vaterite (hexagonal), aragonite (orthogonal), and calcite (rhombohedral). These crystal forms of calcium carbonate were transformed from amorphous calcium carbonate [45], and their thermal stability increased sequentially [46]. Along with the urease activity increased from 0 to 920 u, SEM images (Figure 5) showed that the crystal

morphology of CaCO_3 changed from cubes of different sizes (probable calcite) to nano rod-like bundles and polyhedral grains and finally over to nano rod-like rhombic bundles and spherical grains. The spherical CaCO_3 phase might be vaterite [47], and similar patterns of CaCO_3 precipitation were observed in MICP-treated sand and soil [27,42].

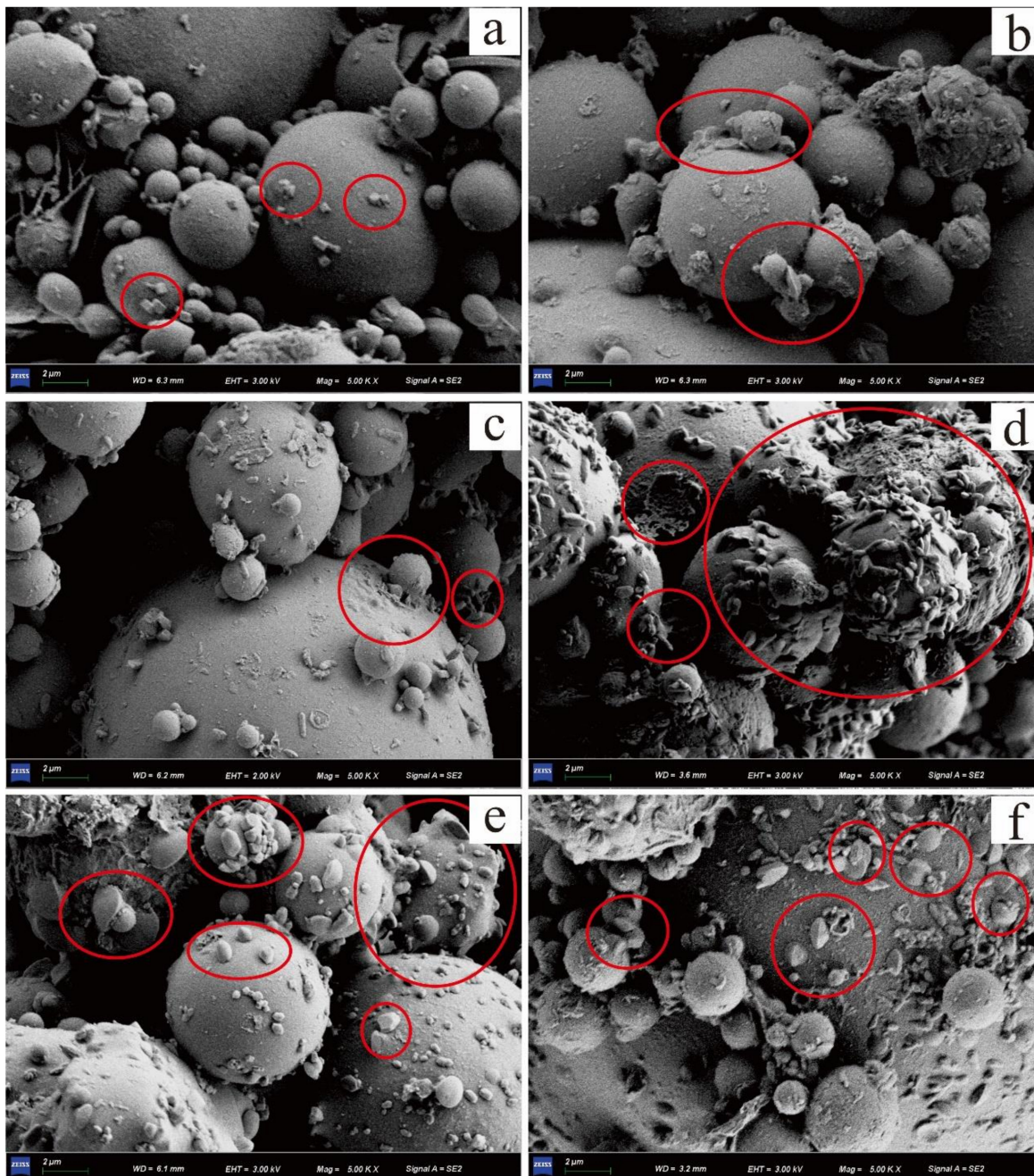


Figure 5. SEM images of FA cured with different treatment solutions ((a): T-0-0-0-0; (b): T-1-0.3-460-0; (c): T-0-0-0-0.6; (d): T-1-0.3-4.6-0.6; (e): T-1-0.3-460-0.6; (f): T-1-0.3-920-0.6). (a): the FA is loose, and a limited number of small calcium carbonate crystals on the surface of the FA particles; (b): the pore spaces between FA particles are slightly decreased, and the calcium carbonate crystals on the surface of the particles become slightly larger; (c): a small number of gelatinous materials were distributed on the surface of FA particles; (d): the FA particles are wrapped and cemented by a large amount of calcium carbonate crystals and gelatinous materials; (e): the calcium carbonate crystals on the surface of FA particles become larger, and most of them are in the shape of polyhedral grains; (f): the calcium carbonate crystals on the surface of FA particles are in the shape of nano rod-like rhombic bundles.

It has been shown that the growth kinetics of vaterite was superior to calcite at high urease activity in the MICP process, while the crystallization of calcite was predominant at low urease activity [35], which also explained the fact that the UCS of the samples treated with EICP-PAM increased by only 3.13% when the urease activity increased from 460 u to 920 u. However, the UCS of these samples increased by 63.05% when the urease activity increased from 46 u to 92 u.

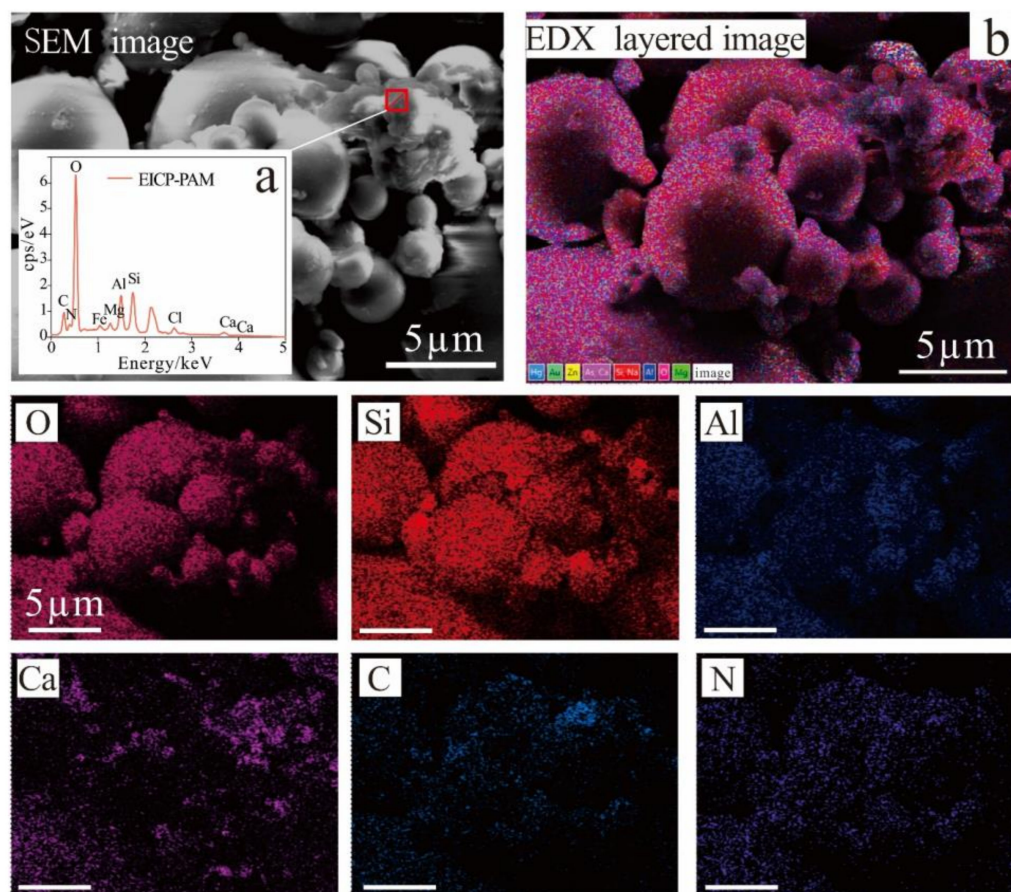


Figure 6. SEM images and EDX mapping of FA treated with EICP. The red box marks the examined area, and the inset (a) shows the line scan result of the marked nanoparticle. On the right and down (b), the corresponding EDX signals for O, Si, Al, Ca, C, and N are shown.

4. Conclusions

The study investigated the consolidation characteristics of FA by EICP mineralization technology, aiming to develop an effective and environmentally friendly technique for particle solidification and wind resistance of FA. The following conclusions were obtained:

- (1) The surface strength, structural stability, and resistance to wind erosion of FA significantly improved with a large number of crystals of CaCO_3 formed by appropriate increases in urea concentration and urease activity.
- (2) The EICP-PAM technique combined the CaCO_3 cementation formed in the EICP process with the hydrogel network immobilization produced by PAM to generate an organic-inorganic composite FA curing agent, which improved the brittle damage characteristics of the samples cured with EICP and made the cured samples have a better ductility.
- (3) Taking into account the economic cost of FA curing, when the CaCl_2 concentration was kept constant (0.3 mo/L), the optimum urea concentration and urease activity were: 1 mo/L and 92 u, respectively, and at this dose, the UCS and wind erosion rate of the sample were 540.9 kPa and 2.905 $\text{mg}/(\text{m}^2 \cdot \text{min})$ respectively. When 0.6 g/L PAM was

added to the treatment solution, the UCS of the samples increased to 908.1 kPa, and the wind erosion rate decreased to $1.992 \text{ mg}/(\text{m}^2 \cdot \text{min})$.

In addition to urease activity and treatment solution ratio, the influence on the curing effect of EICP should be further investigated in terms of optimizing the curing process, improving the reaction efficiency, and selecting and blending the modified materials reasonably (e.g., in this study, the impact of PAM concentration on the curing effect was still lack of research). In conclusion, the EICP was a promising technique for resisting wind erosion in FA sites.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13020185/s1>, Figure S1. XRD patterns of fly ash; Figure S2. Particle size distribution curve of fly ash; Table S1. Major element (wt %) and trace element ($\mu\text{g/g}$) compositions of fly ash; Table S2. Unconfined compressive strength of samples cured with different treatment solutions; Table S3. Particle size distribution of the agglomerates formed by the solidification of fly ash with different solutions; Table S4. Wind erosion rate of samples treated with different solution ($\text{mg}/(\text{m}^2 \cdot \text{min})$); Table S5. Percentages of elements in FA before and after treated with EICP.

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