Inhibition of Efflorescence in Na-Based Geopolymer Inorganic Coating

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ABSTRACT: Coating is one of the most important high-value-added application cases in geopolymer materials. However, efflorescence can easily cause discoloration and reduce the esthetic impression of the coating surface, thus limiting its application; hence, inhibition of efflorescence is one of the most important techniques in the application of geopolymer coatings. Efflorescence is a spontaneous behavior in a Na-based geopolymer, involving the migration of soluble alkalis. Alkalis are dissolved by water and diffuse to the material surface through nocuous pores, and then react with CO₂ to produce white carbonate products. To inhibit efflorescence in geopolymer coating, this article reports a structure modification method using polydimethyl siloxane (PS) and mica. To explore the inhibition mechanism, the effects of PS and mica on the pore structure, water absorption, alkali leaching, and efflorescence product were investigated. The experimental results showed that a harmful pore structure and instinctive water absorption of the geopolymer strongly contributed to efflorescence. PS and mica could reduce the pore size distribution and porosity and are helpful to establish a waterproof structure, leading to water absorption and the alkali leaching rate being significantly suppressed. Both high water glass and water content play a critical role in the increase of efflorescence, but even under a high content of water glass and water used in geopolymer coating, this method shows an 80–90% efflorescence reduction, which is much higher than that of other studies. In practical engineering, when the geopolymer coating is applied after modification, even if it is exposed to the field environment for a long time, there is no efflorescence deposit on the coating surface. It is feasible to limit water ingestion in a geopolymer, which effectively blocks the efflorescence reaction process. This method is simple and practical and can be applied in practical engineering applications of geopolymer coatings conveniently.

1. INTRODUCTION

Inorganic coatings made of film-forming materials (for example, silicate and silica sol), pigments, and fillers have good permeability, durability, and environmental protection properties.¹ It is important that the inorganic coating does not contain any organic solvents, volatile organic compounds (VOCs), and toxic emissions of harmful substances.

Geopolymer is a kind of alkali-activated inorganic material produced by the reaction between an alkaline solution (usually sodium silicate or hydroxides) and solid aluminosilicates. It is widely concerned due to its high-temperature resistance, strong bonding force, excellent durability, good chemical corrosion resistance, environmental friendliness, etc.¹−⁴ In recent decades, a number of studies have been focused on the practical application process of geopolymers;⁵−⁷ the geopolymer used as a coating is one such practical application case with promising commercial potential.¹,⁸−¹¹ Compared with traditional organic coatings, geopolymer coatings have the advantages of excellent aging resistance, good chemical–physical corrosiveness, no volatile organic compound emissions, as well as low cost. However, up to now, geopolymer coating has not been widely used. In fact, surface efflorescence is now considered to be one of the most important problems encountered during the application of geopolymer coating.¹,¹² Geopolymers, particularly those produced by high alkali oxides, may suffer from unsightly surface efflorescence owing to unreacted residual sodium oxide in the materials.¹²−¹⁴ This will not only cause discoloration and reduce the surface’s esthetic impression but also lead to serious physical–chemical reduction.¹⁵ Many studies have agreed that efflorescence of geopolymer results due to the use of a high-concentration alkaline solution as activator in the manufacture process.⁶,¹⁵−¹⁷

The excessive alkali oxides in geopolymers diffused by water move upward through the geopolymer matrix by the pore structure action and evaporate from its surface, resulting in the surface being enriched in alkali cations, which are presented in
the pore solution, and then reacting with CO₂ in the air and forming white carbonate deposits on the surface.¹⁶,¹⁷

Recent studies have explored the eflorescence mechanism of geopolymers. Theoretically, geopolymers activated by any type of alkali metal will encounter the eflorescence problem, but the eflorescence degree may not be the same. By comparing the most commonly used alkali metals ([Na⁺] and [K⁺]), it is found that the eflorescence in Na-based geopolymer is more extensive than that of K-based geopolymer due to the lower polycondensation rate and smaller cation size of [Na⁺].¹⁸,¹⁹ meaning that eflorescence inhibition in Na-based geopolymer is more difficult. It is well known that the gel structures of geopolymers are the co-polymerization units of [AlO₄] and [SiO₄] tetrahedrons connected by common [O] atoms. Within the tetrahedral silicate network, a number of the tetrahedral positions are occupied by [Al³⁺] ions, causing charge loss, which is balanced by the positive ions of the alkali in the skeleton cavity. He¹⁹ studied the effect of Si/Al ratio on the eflorescence behavior of geopolymers and revealed that the geopolymer with Si/Al = 4.0 shows higher eflorescence production than that of the geopolymer with a Si/Al ratio of 2.0. Similarly, a study¹⁷ found that the formation of [AlO₄] tetrahedron in the geopolymer gel structure increases when a pumice-type natural pozzolan or an Al-rich mixture is combined with the geopolymer, which leads to the improvement of the immobilization of sodium ions in the geopolymer matrix, and it is more susceptible to compositional fluctuation.²⁰

Therefore, developing a simple and practical method that can effectively inhibit eflorescence of geopolymer coating is urgently needed, as it is of great significance for further popularization and application of geopolymer coatings.²¹

It is well known that the eflorescence of a geopolymer involves the migration of the alkali substance, and in such a reaction process, water can be regarded as the migration medium and pore structure as the transporting pathway.¹⁶,¹⁷ Hence, it can be reasonably assumed that eflorescence can be inhibited by restraining water ingestion, making the geopolymer coating hydrophobic, thus disrupting the eflorescence reaction process. In this work, the key issue for eflorescence inhibition focused on how to immobilize alkalis in the geopolymer using super fill mica and hydrophobic siloxane. Microstructure analysis, particle size analysis, water absorption, and alkali leaching test were performed to verify the inhibition ability. In addition, X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), and scanning electron microscopy (SEM) were also used to further understand the corrosion inhibition mechanism. Furthermore, to show the possibility in practical applications, a geopolymer decorative coating for a bare wall in a field environment was conducted.

2. EXPERIMENTS AND MATERIALS

2.1. Materials. The primary raw materials used in this study were provided by local suppliers in China. Ground granulated blast furnace slag was obtained from Beihai Chengde Group; mica was purchased from Yuhang Jiacheng Inorganic Mining Industry. The chemical compositions of slag and mica are listed in Table 1, which were obtained by energy-dispersive X-ray fluorescence (XRF) spectrometry on an Axios instrument. The chemical components of slag and mica are listed in Table 1. Figure 1 shows the particle size distribution of mica and slag.

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c01919)  
**Figure 1.** Particle size distribution of mica and slag.
Table 2. Mixed Proportions of Samples

| mix name | W/S (%) | PS/TP (%) | M/TP (%) | W/TP (%) | H₂O/Na₂O |
|----------|---------|-----------|----------|----------|----------|
| RS       | 20      | 0.0       | 0.0      | 0.30     | 23.7028  |
| O1       | 20      | 0.5       | 0.0      | 0.30     | 23.7028  |
| O2       | 20      | 1.0       | 0.0      | 0.30     | 23.7028  |
| O3       | 20      | 1.5       | 0.0      | 0.30     | 23.7028  |
| O4       | 20      | 2.0       | 0.0      | 0.30     | 23.7028  |
| M1       | 20      | 2.0       | 5.0      | 0.30     | 23.7028  |
| M2       | 20      | 2.0       | 10.0     | 0.30     | 23.7028  |
| M3       | 20      | 2.0       | 15.0     | 0.30     | 23.7028  |
| M4       | 20      | 2.0       | 20.0     | 0.30     | 23.7028  |
| WG12     | 20      | 2.0       | 20.0     | 0.30     | 34.8985  |
| WG28     | 20      | 2.0       | 20.0     | 0.30     | 18.3171  |
| WG36     | 20      | 2.0       | 20.0     | 0.30     | 15.1505  |
| WG44     | 20      | 2.0       | 20.0     | 0.30     | 13.0658  |
| W/P20    | 20      | 2.0       | 20.0     | 0.20     | 16.6623  |
| W/P25    | 20      | 2.0       | 20.0     | 0.35     | 20.1826  |
| W/P35    | 20      | 2.0       | 20.0     | 0.35     | 27.2230  |
| W/P40    | 20      | 2.0       | 20.0     | 0.40     | 30.7432  |

Note: W/S, PS/TP, M/TP, and W/TP were marked for water glass/slagoil/powders by mass, respectively. Powders included slag, mica, and water glass. H₂O/Na₂O was noted as the mole ratio of H₂O/Na₂O of samples.

Figure 2. SEM of mica.

2.2. Na-Based Geopolymer Coating Preparation. Table 2 shows a mixed proportion of geopolymer coating samples. Figure 3 is a schematic diagram illustrating the coating preparation process using powder technology. The slag, water glass, and mica were mixed together in a blender, and then water and PS were added to make them even and used as coatings. Further, 1.5 g geopolymer coating was brushed on a Q235 Fe sheet with dimensions of 30 × 50 mm² using the weighing method. After being cured at 25 °C for 7 days, the uncoated surfaces of the Q235 Fe sheet were carefully sealed using epoxy resin. To intensify the efflorescence tendency, an accelerated efflorescence experiment was conducted in this study. The coating samples were immersed in distilled water for 7 h and then further cured in a concrete carbonization test chamber at 25 °C under a 20% CO₂ atmosphere for 7 days. After 7 days of accelerated carbonization curing, the samples were removed from the carbonization test chamber and exposed to the ambient environment to produce efflorescence. The compressive strength test was carried out by pouring the geopolymer paste into a cubic mold with dimensions of 20 × 20 × 20 mm³. In addition, as shown in Figure 3, appropriate amounts of additives (titanium dioxide and emulsion powder) were added to prepare a decorative geopolymer coating, which was brushed on a bare wall in a field environment.

2.3. Sample Characterization. 2.3.1. Efflorescence Analysis. The efflorescence products were scraped from the coating surface to characterize their chemical compositions using XRD on a Rigaku MiniFlex 600 instrument with Ni-filtered Cu Kα radiation. The instrument was operated at 40 kV and 15 mA with a dwell time of 3 s and a step size of 0.020°. The efflorescence production was reflected by [Na⁺] content. The efflorescence products on the coating surface were washed using the ultrasonic washer with 25 g of distilled water, the cleaning solutions were titrated by the acid–base titration method according to Chinese Groundwater Quality Inspection on method DZT 0064.49-1993, and the chemical equation of [Na⁺] content titration was calculated.

2.3.2. Water Absorption and Leaching Test. The water absorption of the geopolymer coating was measured after curing at 25 °C for 7 days. Samples were predried in a vacuum freeze dryer for 1 day, then immersed in distilled water, and the mass increase in the soaking process was recorded by weighing. Water absorption was evaluated from the relationship described in eq 1.

\[
\text{water absorption} = \left( \frac{m_2 - m_1}{m_1} \right) \times 100\% 
\]

where \(m_1\) is the mass of the sample after drying in vacuum for 1 day and \(m_2\) is the mass of the sample after immersion.

The predried geopolymer was cracked and filtered with a 60 mesh sieve and then leached in distilled water at a particle/distilled water mass ratio of 1/100. The leachate was diluted with distilled water at a mass ratio of 1/25 and then subjected to a pH test with a pH-testing device, PHS-3C.

2.3.3. Microstructure Analysis. The morphology of the geopolymer was analyzed using a SEM (S-3400N, Japan) device with an acceleration voltage of 15 kV. The geopolymer coating was cut and then coated with gold prior to the SEM test. The microstructure of the geopolymer was studied using the nitrogen absorption method on a surface area and the porosity device Gemini VII (Micromeritics Instrument Corp.), and the average pore size was calculated by the Barrett–Joyner–Halenda (BJH) method. The samples were cut and crushed to the same size and were dried in a vacuum freeze drier for 12 h before characterization.

2.3.4. Engineering Application. According to the preparation process in Figure 3, geopolymer coatings with and without structure modification were produced and brushed on an
exterior wall with dimensions of $3 \times 3$ m$^2$ in a field environment in Nanning City, Guangxi Province, China (yearly temperature 21.6, humidity 79%). The appearance of the coating surface was recorded by a camera (iPhone8 plus).

3. RESULTS AND DISCUSSION

3.1. Mechanical Strength and XRD. The XRD patterns of mica as well as the representative samples of RS, O4, and M4 after being cured for 28 days are shown in Figure 4. The main crystalline phases of mica are SiO$_2$ (quartz) and muscovite ($K_2O\cdot3(Al_2O_3)\cdot6(SiO_2)\cdot2(H_2O)$); mica shows no obvious broad hump, indicating that large quantities of amorphous phases do not exist. The sample of M4 composited with mica shows similar patterns with the presence of the characteristic peaks from mica, confirming that the crystalline phases acted as inactive fillers in the geopolymer networks. A broad bump of $22\sim35^\circ$ can be seen both in the sample before (RS) and after (O4) PS addition, which indicates that PS in the geopolymer networks did not take part to form new chemical compounds, as the broad amorphous peak appears in the same position.

Figure 4 shows the mechanical strength development of the geopolymer composited with PS and mica. It can be seen that no significant mechanical change was observed when PS was added; only around 10% strength reduction was calculated both at 3 and 28 days after a maximum of 2% PS was added. Such a slight decrease in strength was less likely to be responsible for the reaction of PS with aluminosilicate in the geopolymerization process but was probably related to the hydrophobic performance of PS, which indicated that PS might adsorb on a part of the slag grain surface, thus reducing the wetting and dissolving extent by the alkaline solution. It also can be found that a clear strength reduction was exhibited with the increasing content of mica, which resulted in around 35% strength reduction at 28 days after a maximum of 20% mica compositing. It is well known that smaller particles can usually be used as fillers to achieve higher mechanical strength; Wang$^{21}$ reported that 28 days of compressive strength can be improved by about 40% when adding 2% amorphous nanosilicate to the geopolymer. But this result is completely contrary to previous studies. The reason for the reduction caused by the use of mica can be attributed to the following: as verified in XRD results, mica used as an inactive filler cannot be alkali-activated by water glass and fails to improve gel formation. On the other hand, mica definitely diluted the geopolymer binder content due to the large use in this study. However, it should be noted that high mechanical strength is not always a good thing, for example, sometimes high bonding strength of the geopolymer coating may cause peeling; the geopolymer coating and the putty surface will pull out of the wall together.$^{22}$ The 28 days’ compressive strength of M4 is 43 MPa, which is very close to the OPC 425 cement. This strength value can provide enough high-strength requirements for coating use.$^{23}$

3.2. Water Absorption and Leachate Test. Geopolymers possess an inherent hydrophilic feature due to the multiple hydroxyl groups in their chemical structure, and water absorption can be considered as directly related to the porosity, which provides capillary volume for water ingestion. The effects of PS and mica on the waterproof performance of the geopolymer coatings were accessed by the water absorption test. The results of Figure 6 show that the water absorption of the plain geopolymer coating RS was significantly higher than that of the modified samples, and RS showed the fastest water absorption rate with time. However, the water absorption capacity was significantly inhibited when PS and mica were added; the absorption capacity of water decreased from 6.57% (RS) to 2.00% (O4) with the addition of 2% PS and further decreased to 0.60% when 20% mica was composited. These results suggested that the use of PS and mica can effectively reduce the water absorption of geopolymer coating, which might be attributed to the fact that PS, as a hydrophobic material, effectively endows the geopolymer coating with waterproof performance, and the other reason is that mica is most likely to fill and cover the pore space of the geopolymer coating.

The alkalis ([Na$^+$], [OH$^-$]) leaching from the geopolymer coating can be reflected by the pH value. To understand the influence of PS and mica on the leaching behavior of alkalis in the geopolymer coating, the leachates were tested by pH measurement. As shown in Figure 7, RS exhibited the highest initial pH value of 11.26, and after 4 h of leaching, the pH
value reached 11.45 rapidly. As expected, the use of PS and mica obviously reduced the initial pH value and increase rate; after being leached for 96 h, sample O4 with 2% PS addition showed a pH value of 11.05 and M4 showed a pH value of 10.88 after further compositing with 20% mica. These results revealed that the vigorous alkali leaching behavior of the geopolymer was strongly restrained by the addition of mica and PS. Obviously, the most important reasons for the decrease of alkali leaching is the reduction of water absorption after adding PS and mica and the improvement of hydrophobicity increasing the mass transfer, thus strongly hindering the diffusion of alkalis in water.

3.3. Microstructure Analysis. The pore structure of the geopolymer coating plays a critical role in water ingestion. Nocuous pores provide transporting channels for alkali substance when water molecules invade, resulting in [Na+] and [OH−] migrating out from the interior of the geopolymer to the surface by dissolution and diffusion effect caused by water. The pore size of the geopolymer usually consists of two types: gel pores, formed in the interstices of the aluminosilicate gel phase (<10 nm), and capillary pores, the remnants of the original water-filled space (10–100 nm).24,25 Figure 8 shows the pore size distribution and porosity of geopolymer coating obtained from the most representative samples RS, O4, and M4. As shown in Figure 8A, sample RS possessed the largest pore size distribution of 2–90 nm, but after adding 2% PS, the pore size distribution decreased to 2–60 nm in O4 and further decreased to 2–40 nm after compositing 20% mica in M4. The average pore size was calculated by the BJH method and the results show that M4 had the smallest average pore size of 6.50 nm compared to 10.0 nm in O4 and 17.5 nm in RS. Moreover, a significant reduction of capillary pore volume was also observed after the structure was modified (Figure 8B). Such results indicated that mica would effectively reduce the porosity of the geopolymer coating. On the other hand, the use of PS also slightly refined the microstructural property, which is probably because PS reduces the friction between the slag grains during dispersed process, leading to the densification effect between slag grains, and PS, as a soft elastic organic molecule, might be evenly filled in the capillary pores.

The SEM images of the geopolymer coating of M4 and RS are shown in Figure 9. From the micrographs, it can be seen that multiple incomplete reaction slag grains are clearly observed on the surface of the RS sample (Figure 9E), which corresponds to the poor compact surface with lots of nocuous pores, and the slag grains bridge together to create large voids. This phenomenon can be attributed to the following. The geopolymer coating is usually a relatively thin layer, and thus the water escapes quickly from the coating body to the air after being brushed on the substrates, resulting in the incomplete dissolution of slag grains during the alkali dissolving process. This explanation was supported by other studies that had found that low internal humidity caused the lack of pore solution for the dissolution of aluminosilicate.26 Figure 9F–H reveals a dense C-S-H/A-S-H gel with microcracks and incompletely reacted slag particles embedded in the fracture structure of RS. These clear microcracks found in Figure 9G were a result of the shrinkage of the gels after the evaporation of crystal water in the gel cavity;27 however, the severe cracks observed in Figure 9H might be due to the polishing process because of the instinctive brittleness of the geopolymer.28 A noticeable change can be found when mica and PS were added. Most of the ultrafine mica particles were observed to be filled in the surroundings of slag grains (Figure 9C). Geopolymer adhesive-bonded the mica particles integrally as a cementitious matrix without cracks. Because of the flake structure of mica, voids were significantly filled by mica layer by layer (Figure 9D), which resulted in a more compact structure with a few large pores and fracture on the surface (Figure 9A,B).

3.4. Efflorescence Behavior Analysis and Test. To analyze the chemical composition of efflorescence, the white deposit was collected and analyzed using XRD. From Figure 10C, it is noted that the chemical composition of efflorescence is \( \text{NaHCO}_3\cdot7\text{H}_2\text{O} \). However, previous studies reported that the formation of efflorescence is \( \text{Na}_2\text{CO}_3\cdot7\text{H}_2\text{O} \).16 These results can be attributed to the accelerated carbonization test (20%) used in this study. Excessive amounts of \( \text{CO}_2 \) were provided during the carbonization process, causing the formation of \( \text{NaHCO}_3 \) to prevail, as reported by a similar study.18 However, when efflorescence was produced under atmospheric conditions, due to the relatively low concentration of \( \text{CO}_2 \) (0.03–0.04%), the formation of \( \text{Na}_2\text{CO}_3 \) was favored.16,28 However, residual unreacted [Na+] and [OH−]...
may still be present in the coating surface. Importantly, efflorescence (Figure 10A,B) is a kind of plagioclase crystal. Figure 10A shows that efflorescence occurred in the pore center instead of the surface of the slag particle, which further confirmed that efflorescence was closely related to the migration of [Na⁺] and [OH⁻] from the geopolymer. The pore structure of the coating provided a transporting pathway and space sites for carbonation deposits. Therefore, the efflorescence reaction can be described as eqs 2 and 3

\[
\text{CO}_2 (g) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 (aq) \rightleftharpoons [\text{H}^+] (aq) + [\text{HCO}_3^-] (aq)
\]

(2)

\[
[\text{H}^+] (aq) + [\text{HCO}_3^-] (aq) + [\text{CO}_3^{2-}] (aq) + [\text{OH}^-] + [\text{Na}^+] \rightleftharpoons \text{Na}_2\text{CO}_3\cdot7\text{H}_2\text{O} (s) + \text{NaHCO}_3\cdot7\text{H}_2\text{O} (s)
\]

(3)

To investigate the efflorescence extent of geopolymer coating after structure modification, the efflorescence products of the representative samples RS and M4 were washed and titrated. Figure 11 shows the efflorescence mass reflected by [Na⁺] concentration with carbonization evolution. It can be seen that RS showed intense efflorescence with the carbonization evolution, and [Na⁺] concentration was still obtained as high as 45.50 mg/L even after five times of carbonization, suggesting that the efflorescence of geopolymer coating is a long-lasting process, which cannot be avoided by just washing with water. It can also be found that efflorescence was effectively restrained after structure modification; compared to the initial efflorescence of 94.80 mL in RS, only 10.17 mg/L was obtained in M4. Furthermore, the [Na⁺] concentration of M4 was about 10 times lower than that of RS during the whole experiment. Many studies agreed that efflorescence can be relieved by improving A-S-H gel by adding Al-rich aluminosilicates,6,16,19 however, this method is very limited because alumina chemical formation may not be the same in different aluminosilicates and thus they may change the geopolymerization and form a different type of gel structure.17 A similar study was reported. Wang found that efflorescence can be reduced to nearly 55% using 2% amorphous nanosilica, which was a result of the filling effect.21 Huang and Wang found that 5A zeolite could fix [Na⁺] by ion exchange; compositing 15% zeolite in the geopolymer led to a 44% reduction of efflorescence.20,29 In comparison, a much higher efflorescence decrease (80−90%) was found in this study, and this efficiency can be stably maintained even in prolonged carbonization times. It can be concluded that, compared to the method of directly fixing [Na⁺] in the geopolymer gel, the direct inhibition of water carrying [Na⁺] to the surface showed a more effective inhibition extent.

3.5. Inhibition Mechanism of Efflorescence. Figure 12 presents a schematic diagram illustrating the efflorescence inhibition mechanism of the modified structure. Initially, during the mixing of the fresh paste, PS was adsorbed on the surface of mica and slag particles, which reduced the friction between these particles. Meanwhile, mica was used as a filler padded in the gap of the slag particles, forming a compact paste and reduced voids. Second, in the solidifying process, water quickly evaporated from the paste’s body, which resulted in the void volume of the capillary pore, but hydrophobic PS could not evaporate, and therefore it remained in the void...
volume formed by water evaporation, leading to the enrichment of PS in the pore wall. As a result, a compact structure with lower pore size, porosity, as well as excellent hydrophobicity was established, which was beneficial for hindering water diffusing into the binder matrix to transport alkalis. Therefore, the efflorescence reaction process described in eq 2 was limited.

3.6. Efflorescence Inhibition Efficiency Analysis. Geopolymer coatings now are produced with a wide range of formulations and high alkali concentration, and a large amount of water/powders was often used in the production process to obtain a pleasing chemical—physical performance. However, this highly enhances the efflorescence risk, as water glass and water content strongly affect the microstructure of the geopolymer. Therefore, examining the efficiency of efflorescence inhibition under various ratios of water glass and water content is necessary. Figure 13A,C shows the effect of water glass on the pore structure, which indicated that pore size distribution and porosity were reduced with the increasing use of water glass because high alkalinity was beneficial for geopolymerization to form a denser structure. However, there was no doubt that the higher the content of water glass used, the higher the concentration of [Na+] that would be left in the samples. In addition, it can be noted that the porosity enlarged with the increasing mass ratio of water/powders (Figure 13B,D), which can be attributed to the evaporation of residual water from the capillary pore during the hardening process. The influence of the water glass and water content on efflorescence mass was reflected by [Na+] concentration, and the results are shown in Figures 14 and 15, respectively. It can be seen in Figure 14 that [Na+] concentration improved with the increasing use of water glass but decreased with the evolution of carbonization. On the other hand, as shown in...
Figure 15, [Na+] concentration was enhanced with the increasing use of water but also decreased with the evolution of carbonization. To give an intuitive efﬂorescence inhibition efﬁciency, the cumulative efﬂorescence mass was calculated and is listed in Table 3. It can be seen that water glass used in sample WG44 was about two times higher than that of RS, but the cumulative [Na+] concentration of WG44 was only 44% compared to that of RS. Compared to water glass, the efﬂorescence extent affected by water content is lesser, as the contrast ratio increased from 8.75 to 15.40% only when water/powders were increased from 20 to 40%. Such results conﬁrmed the high efﬁciency of the structure modiﬁcation for efﬂorescence inhibition in geopolymer coating.

3.7. Engineering Application. A geopolymer decorative coating with and without structure modiﬁcation treatment was applied in real engineering on a bare wall in a ﬁeld environment. The coatings were fully sprayed with water after being cured for 7 days. Figure 16A–C shows the surface appearance of the coating without structure modiﬁcation treatment. The visible formation of efﬂorescence on the coating surface after being exposed for 3 days can be seen, and the white products thickened after 7 days (Figure 16B). When the exposure time was extended, as shown in Figure 16C, a dense efﬂorescence layer can be seen, while the coating surface was damaged. In contrast, after the structure modiﬁcation, the efﬂorescence deposits on the coating surface cannot be seen by the naked eye (Figure 16D,E), and the appearance almost stayed the same even after 28 days of exposure (Figure 16F). The result demonstrated the possibility of using structure modiﬁcation for efﬂorescence inhibition in practical applications of geopolymer coating.

Figure 16. Surface photos of geopolymer decorative coating used in real engineering applications: surface appearance of the coating without structure treatment after being cured for 3 days (A), 7 days (B), and 28 days (C) and surface appearance of the coating with structure treatment after being cured for 3 days (D), 7 days (E), and 28 days (F).

Table 3. Efﬂorescence Extent Comparisons of the Different Mass Ratios of Water Glass/Slag and Water/Powders

| mix name | RS       | WG12     | WG20(M4) | WG28     | WG36     | WG44     |
|----------|----------|----------|----------|----------|----------|----------|
| cumulative mass (mg/L) | 323.00   | 33.86    | 32.90    | 74.50    | 108.46   | 133.77   |
| contrast ratio (%)     | 100.00   | 10.48    | 10.19    | 23.07    | 33.58    | 41.41    |

| mix name | RS       | W/P20    | W/P25    | W/P30(M4) | W/P35    | W/P40    |
|----------|----------|----------|----------|-----------|----------|----------|
| cumulative mass (mg/L) | 323.00   | 28.27    | 32.23    | 32.90     | 45.92    | 49.75    |
| contrast ratio (%)     | 100.00   | 8.75     | 9.98     | 10.19     | 14.22    | 15.40    |

Note: the contrast ratio was marked for the cumulative [Na+] concentration of the experimental sample after ﬁve times of carbonization divided by that of the reference sample (RS).

4. CONCLUSIONS

In this study, a simple and effective structure modiﬁcation method using PS and mica for efﬂorescence inhibition in geopolymer coating was proposed. The inhibition efﬁciency was also investigated with various ratios of water glass and water content. The experimental results found that the geopolymer coating surface had a large number of voids and micropores due to incomplete geopolymerization, which could provide a pathway for water ingestion to induce efﬂorescence. The poor compact structure problem could be solved by the composition of mica and PS. Mica and PS could not only ﬁll in the nocuous pores but also endow the geopolymer coating with excellent waterproof performance and strongly inhibit the water absorption and alkali leaching rate so that the dissolution and diffusion of alkalis were hindered. Mica and PS did not react with the geopolymer and reduced the compressive strength, but 28 days’ compressive strength of the geopolymer after the maximum composition with 2% PS and 20% mica still reached the maximum value of 43 MPa, which well meets the strength requirements for coating. Even the geopolymer coating with a high content of water glass and water can reduce the weathering quality by 80–90%. This method was successfully applied to practical engineering application of geopolymer coating and could stably inhibit efﬂorescence under long-term exposure. This work is of great engineering signiﬁcance for the popularization and application of geopolymer coating, and its efﬂorescence inhibition mechanism has important research signiﬁcance and application potential.
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