Review on the Adhesion of Geopolymer Coatings
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ABSTRACT: Geopolymers are considered to be green materials with excellent fire resistance performance and potential substitutes for ordinary Portland cement (OPC). This review article focuses on the adhesion of geopolymer coatings subjected to elevated temperature. Their high adhesion strength is the basis for geopolymers being used as coating materials to work with the substrate. The adhesion strength is related to many factors, such as chemical composition of the raw materials, the formulation of the geopolymer, substrate type, surface roughness of the substrate, etc. The Si/Al ratio has different effects on compressive strength and bonding strength. The water content affects the polymerization process—the adhesion strength decreases with increasing water content. Careful tailoring of the mix ratio design is essential to make the geopolymer coating have excellent adhesive performance. These mix design factors include Si/Al ratio, Al/Na ratio, water content, precursor type, alkali cation type, curing conditions, etc.

1. INTRODUCTION
Fires occurred frequently in recent years, causing major casualties and property losses. Although there are some advanced technologies and measures to improve the fire resistance of structures, they are usually expensive and cannot be widely used in engineering structures. A fire-resistant and environmentally friendly material is urgently needed. Geopolymer materials have the advantages of a wide selection of raw materials, energy-saving features, simple technology, and environmentally friendly nature. They have the same mechanical properties as ceramics. In view of the excellent mechanics and fire resistance performance of geopolymers, the application of geopolymers is becoming more and more extensive, such as geopolymer coatings, geopolymer cements and concretes, geopolymer fire resistant and insulation materials, and geopolymer refractory materials.

In order to better promote the application of geopolymers in engineering, it is necessary to conduct an in-depth literature review on the adhesion of geopolymer coatings exposed to elevated temperatures.

2. ADHESION BOND BEHAVIOR

2.1. Adhesion Strength. A number of studies on the corrosion and fire protective behavior of geopolymer coatings over substrates (such as wood, steel, and concrete) are listed in Table 1. The current research mainly focus on the fire-resistant time, thermal conductivity, and thermogravimetric analysis of the geopolymer coating itself. Few works of literature have studied the surface adhesive properties of geopolymer coatings to substrates.

The high adhesion strength of geopolymers is the basis for their use as coating materials to work with the substrate. The polymerization of a geopolymer is very rapid, so geopolymers can obtain high strength in the initial stage of curing.1 The bonding strength of these coatings increases to a maximum within 7 days and then becomes constant.2 Therefore, these coatings do not need to be cured for a long time, which can facilitate construction projects. Khan et al.3 reported that these coatings can gain maximum strength during the first 3 days of curing and the adhesion strength remains almost constant even when the curing is extend to 180 days.

2.2. Influencing Factors. 2.2.1. Si/Al. The Si/Al ratio is a vital factor affecting the adhesion properties of geopolymers. Many researchers8–12 have reported the effect of the Si/Al ratio on compressive strength. From previous studies, it is found that Si/Al has different effects on compressive strength and bonding strength, as shown in Figure 1 (The solid lines represent unconfined compressive strength (UCS) values, and the pink dotted line represents ultimate adhesion strength (UAS) values). The magnitude of compressive strength is

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related to many factors, such as raw material type, alkali stimulant, etc. The development of this curve is similar, when the value of Si/Al is around 1.9 and the UCS value reaches a maximum. As a comparison, bonding strength does not reach the maximum; in such a case, the bonding strength increases as the Si/Al ratio rises. Latella et al. showed strong adhesion between steel and a metakaolin based geopolymer when reference to Si:Al = 2 and Na:Al = 1. As a comparison, Temuujin et al. reported that the adhesion was very weak when Si/Al = 1 and 2 and the adhesive strength was >3.5 MPa when Si/Al = 2, 3, 3.5. This inconsistency may be due to different geopolymer preparation processes. Therefore, when the geopolymer is used as a coating material, its composition should be rationally designed, aiming to have a better adhesive properties.

Wan et al. compared the geopolymerization reaction, microstructure, and strength of MK-based geopolymers with respect to Si/Al ratios of 1:1, 1.5:1, 2:1, 3:1, 4:1, and 5:1. SEM images of these geopolymers are show in Figure 2. When Si/Al = 1, a small amount of geopolymer binder and some zeolite cores were observed. Because most of these nuclei are not dispersed in the geopolymer binder, macro- pores are formed. The formation of macropores resulted from most of the undispersed nuclei in the geopolymer binder. It can also be observed from the NMR result and XRD pattern that geopolymers present the feature of high crystalline phase content. When Si/Al = 2, a homogeneous geopolymer binder was found. When Si/Al = 3, derivatives of soluble silicates, such as nesosilicates and silicic acid, were observed in geopolymer binders. When Si/Al = 4, there was no geopolymer binder, and plenty of micropores or mesopores were observed. From above, it was noted that the strength of geopolymers depends on the formation of the N-A-S-H gel, when subject to the UCS values at different Si/Al ratios (Figure 1).

Wan et al. found that soluble silicates can promote the polymerization of alumin monomers and, therefore, promote the dissolution of aluminum from the raw metakaolin, and the rate of the acceleration of polymerization or condensation reaches equilibrium at Si/Al = 2.1. However, excessive soluble silicate will reduce the strength of the geopolymer, which is caused by two factors. (1) A high silicate concentration enhances the formation of Si-rich gel with a high percentage of bridge bonds, resulting in an amorphous geopolymer. (2) Excess silicate could prevent water from evaporating, which is negative to the formation of geopolymer structures. But some researchers found that the addition of soluble silicates could not change the structural stability of geopolymers.

2.2.2. Water Content. The water content significantly affects the bonding strength, setting time, and pore structure of the geopolymer, but it shows no relationship with the fire resistance performance of the geopolymer.

The adhesion strength between the geopolymer coating and the substrate decreases with increasing water content. The water content affects the polymerization process, and high water content leads to the poor curing behavior. Khan et al. reported that when the Na/Al ratio is low, the bond strength is more affected by the water content. This is because the increase in water content will dilute the alkali activator. Temuujin et al. found that high water content will reduce the concentration of dissolved aluminum ions, thus reducing the gelation and hardening of the geopolymer. Khan et al. found that, when the Na/Al ratio is 1 and the water/solid ratio is 0.33, the maximum adhesion (3.8 MPa) is achieved and that the results are comparable to geopolymer coatings containing sodium silicate.

2.3. Steel—Geopolymer Interface. The surface characteristics and contact angle of the substrate, as a prerequisite for

| Table 1. Adhesion Strength of Geopolymer Coatings |
|--------------------------------------------------|
| ref     | geopolymer type | Na/Al | water/solid | Si/Al | max adhesion strength (MPa) | compressive strength | substrate |
|---------|----------------|-------|-------------|-------|-----------------------------|---------------------|-----------|
| Khann et al. | FA-based      | 0.8−1.2 | 0.33     | 1.78  | 3.8                         | steel               |
| Bell et al. | MK-based      | 1     | 0.61      | 1     | 6.8+/−1.4                  | mild steel          |
| Temuujin et al. | MK-based | 1     | 0.45      | 2     | 3.6+/−1.8                  | mild steel          |
| Temuujin et al. | 1     | 0.45      | 2     | 3.6+/−1.8                  | mild steel          |
| Temuujin et al. | FA-based | 1     | 0.35      | 1     | 0.25(0.1)                 | 2.6(0.4)            |
| Temuujin et al. | FA-based | 1     | 0.35      | 2     | 0.5(0.15)                 | 0.8(0.2)            |
| Temuujin et al. | FA-based | 1     | 0.35      | 3     | 2.9(0.1)                  | mild steel          |
| Temuujin et al. | FA-based | 1     | 0.35      | 3.5   | >3.5                      | mild steel          |
| Temuujin et al. | MK-based | 1     | 0.41      | 2.5   | >3.5                      | mild steel          |
| Temuujin et al. | MK-based | 1     | 0.45      | 2.5   | >3.5                      | steel               |
| Temuujin et al. | MK-based | 1     | 0.50      | 2.5   | >3.5                      | steel               |
| Bhardwaj et al. | FA-based | 0.076 | 2.816     | 3.5   |                             | mild steel          |
geopolymer coatings to have good heat resistance and corrosion resistance, have an important influence on the adhesion properties. Problems induced by poor adhesion, such as cracking of the coating, early peeling, and inability to work with the substrate, are often seen. The adhesion between the geopolymer and the matrix is related to many factors, such as chemical composition of the raw materials, the formulation of the geopolymer, substrate type, surface roughness of the substrate, etc.

Mechanical treatment (sand blasting) and chemical treatment (nitrophosphoric acid and silanization) were carried out on steel and aluminum plates, and the bonding strength was determined by methods such as the single- and double-shear, pull-out test, and mixed mode flexural test. Yong et al.22 found a chemical interaction of Al−O−Fe bonds between geopolymer gel and metal substrates. However, Temuujin et al.5 pointed that the bonding adhesion is physical bonding rather than chemical bonding. The fact is that with chemical bonding of Al−O−Fe bonds, geopolymers with a higher Al/Si ratio should have better adhesion, but this is not in agreement with the experimental results. In their experiments, geopolymers with Si/Al ratios = 2.5 contain fewer Al atoms but have better bond strength than geopolymers with Si/Al ratios = 1 and 2. Debarros et al.23 also believed that mechanical treatments were more effective than chemical treatments for both steel and aluminum joints when geopolymers were used as adhesives.

Temuujin et al.5 believed that, since all metal substrates are prepared in the same way, the difference of adhesion strength of various geopolymer compositions upon metals was clearly independent of surface roughness. However, even if the metal surface is treated in the same way, the surface roughness of each substrate is different for a number of reasons such as the time and power of grinding. In the coating industry, many researchers have studied the relationship between substrate surface roughness and bond strength, which provides valuable literature contributions to the body of knowledge about geopolymers as coating materials.

There are many parameters used to characterize roughness, the most common of these is the profile center line roughness parameter Ra.24 On the macroscale, the relationship between Ra and the mechanical properties of the component (bending strength, splitting strength, and bonding strength) can be established, with a confidence level of approximately 0.85.25 On the microscale, researchers established the relationship between Ra and friction coefficient, ultimate load, and wear rate. De Barros et al.26 studied the relationship between substrate roughness and shear strength by shear tests. From the results, to study the relation between the surface roughness and adhesion, multiple parameters are more effective than a single parameter. The confidence level of the multiparameter formula can reach 0.99.

The determination of Ra is limited to the profile centerlines of the substrate surface, which brings the problem that it is difficult to get an appropriate Ra representing the roughness of the substrate surface. Hence, numerous studies have attempted to find new parameters to better characterize the relationship between surface roughness and adhesion properties.27,28 In this way, a new parameter was proposed by Goltsberg et al.,28 which controls the critical contact parameters at yield inception of the coated system, known as the dimensionless coating parameter. It is given by the following equation

$$\chi' = \left( \frac{f}{R} \right)^{0.507}$$

(1)

where the subscripts “co”, “su”, and “c” represent the coating, substrate, and the critical parameters of the combined system. R is a spherical shell of an inner radius, and t means wall thickness.
3. CONCLUSIONS

Numerous researchers have studied the fire resistance performance of geopolymer coatings, mortars, and concretes exposed to high temperatures. Their fire resistance performances are similar, but there are some different aspects.

1. A good adhesive performance of the geopolymer as a coating material is of great significance to work with the substrate. The adhesion strength is related to many factors, such as chemical composition of the raw materials, the formulation of the geopolymer, substrate type, surface roughness of the substrate, etc. The adhesion decreases with an increase of water content. The water content affects the polymerization process, and a high water content leads to poor curing behavior. The bonding mechanism between a geopolymer coating and substrate requires further study.

2. With the rise of the Si/Al ratio, the bonding strength increasing, while the compressive strength goes up first and then decreases. Geopolymers synthesized at various Si/Al ratios have different phases in the geopolymer binder. It is noted that the formation of a geopolymer binder is significant in controlling mechanical strength and thermal performance. Therefore, research on the thermal performance of geopolymer coatings with a high Si/Al ratio will become indispensable.

3. From experiments, adhesive properties could be better characterized by the relative area of the substrate surface. The surface roughness and contact angle of the substrate are vital factors affecting the bonding strength. Multi-scale analyses and characterizations of surface topographies can be used to solve adhesion problems. The influence of the surface roughness and contact angle of the substrate on the adhesion properties of geopolymer coatings needs further study.

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Notes
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