Water resistance of flue gas desulphurization gypsum-fly ash-steel slag composites

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Abstract. Flue gas desulphurization gypsum-fly ash-steel slag (FGD-FA-SS) composites with different mass percentages of NaOH and redispersible polymer powder (RPP) were prepared, and the effects of NaOH and RPP added on the water resistance of composites were researched. The results demonstrated that the addition of NaOH improved the water absorption and softening coefficient of composites due to the production of more hydration products. And RPP could modify the pore structure and decrease the gypsum solubility resulting in the improvement of water resistance. Besides, NaOH and RPP co-doped had a more positive effect on water absorption and softening coefficient of composites compared to NaOH or RPP addition separately which was mainly attributed to the synergistic effect of NaOH and RPP on FGD-FA-SS composites.

1. Introduction
In recent years, a large number of industrial solid wastes such as FGD, FA, and SS have been produced with the rapid development of industrialization which occupy land resources and cause environmental pollutions [1-2]. Therefore, measures must be taken on the utilization of industrial waste solid in large scale. FGD, as a cementitious material, has attracted the attention of researchers owing to its high early strength, low energy consumption, nontoxicity and low density [3-5]. However, it is hard for pure FGD to meet the requirements in building materials application due to its weakness such as low late strength and poor water resistance [6]. FA and SS are also industrial solid wastes that can be added into FGD to improve its weakness owing to pozzolanic activity of FA and potential cementitious action of SS which lead to the production of various hydration products such as the hydrated calcium silicate and hydrated calcium aluminate that can fill pore spaces and reduce the water permeation into the hardened cementitious composites [7-8]. Besides, hydration activity of FA and SS is improved by the addition of NaOH that can destroy the glass phase by increasing the alkalinity of the composites to generate more hydration products, which are beneficial to the improvement of water resistance [9-10]. RPP is an organic copolymer material that is usually produced by spray-drying polymer emulsion containing an anti-caking agent and a colloidal stabilizer. Ma et al. [11] investigated the influence of RPP addition on the waterproof performance of cement-based composites and concluded that adding RPP could significantly improve the water resistance by modifying the pore structure and reducing the water permeation.

Moreover, Pagona et al. [12-13] also drew the same conclusion by testing on the OPC mortar. Hence, it is believed that water resistance of FGD-FA-SS composites has excellent potential to be strengthened by the addition of RPP. Although NaOH and RPP have a beneficial effect on water resistance, few pieces
of research on the impact of NaOH and RPP addition on water resistance properties of FGD-FA-SS composites has been reported.

This paper aimed to enhance the waterproof performance of FGD-FA-SS composites by adding NaOH and RPP and the water resistance was evaluated by water absorption and softening coefficient.

2. Experimental

2.1. Raw materials and treatment

FGD and FA used in this work were collected from Shandong Laiwu Power Plant in China and SS was supplied from Laiwu Iron and Steel Group in China. The chemical compositions of FGD, FA and SS were shown in table 1. The commercially available NaOH and RPP were used in this study to improve the waterproof performance of FGD-FA-SS composites. Before the experiment, the FGD was calcined at 155 ℃ for 200 min in a high temperature industrial furnace and placed at room temperature for 7 days to transform it into hemihydrate gypsum. Besides, the FA and SS were ball-milled using a planetary ball milling machine at a speed of 300 rpm for 6 h before using them to excite hydration activity of FA and SS.

Table 1. The chemical composition of raw materials (wt%).

|     | SO₃  | MgO  | SiO₂  | CaO  | Al₂O₃ | Fe₂O₃ |
|-----|------|------|-------|------|-------|-------|
| FGD | 43.11| 2.01 | 1.45  | 31.80| 0.53  | 0.21  |
| FA  | 0.64 | 0.93 | 47.13 | 4.13 | 40.33 | -     |
| SS  | 1.14 | 4.83 | 15.44 | 46.01| 5.57  | 18.25 |

2.2. Samples preparation and test methods

In this study, the ratio of water-to-binder (FGD-FA-SS composites) was 0.51, and the proportions of FGD, FA, and SS in FGD-FA-SS composites were 7:2:1. Moreover, NaOH and RPP were added with different mass percentages, as shown in table 2. The above raw materials were mixed in a paste mixer at a speed of 140 rpm for 150 s. The samples were formed in a steel mold and demolded after 2 hours. The specimens were cured at room temperature for 28 days.

Table 2. The mixed proportions of FGD-FA-SS composites (wt%).

| Sample | FGD | FA | SS | Water | NaOH | RPP |
|--------|-----|----|----|-------|------|-----|
| A0     | 70  | 20 | 10 | 0.51  | 0    | 0   |
| A1     | 70  | 20 | 10 | 0.51  | 0.5  | 0   |
| A2     | 70  | 20 | 10 | 0.51  | 1.0  | 0   |
| A3     | 70  | 20 | 10 | 0.51  | 1.5  | 0   |
| A4     | 70  | 20 | 10 | 0.51  | 2.0  | 0   |
| A5     | 70  | 20 | 10 | 0.51  | 2.5  | 0   |
| B1     | 70  | 20 | 10 | 0.51  | 0    | 1   |
| B2     | 70  | 20 | 10 | 0.51  | 0    | 2   |
| B3     | 70  | 20 | 10 | 0.51  | 0    | 3   |
| B4     | 70  | 20 | 10 | 0.51  | 0    | 4   |
| B5     | 70  | 20 | 10 | 0.51  | 0    | 5   |
| C1     | 70  | 20 | 10 | 0.51  | 0.5  | 1   |
| C2     | 70  | 20 | 10 | 0.51  | 1.0  | 2   |
| C3     | 70  | 20 | 10 | 0.51  | 1.5  | 3   |
| C4     | 70  | 20 | 10 | 0.51  | 2.0  | 4   |
| C5     | 70  | 20 | 10 | 0.51  | 2.5  | 5   |
The water resistance of composites was evaluated by water absorption at 2 hours and 24 hours and softening coefficient in this paper. The water absorption of samples was calculated using the following equation:

\[
W = \frac{(G_2 - G_1)}{G_1} \times 100\% 
\]  

where \(W\) is water absorption of samples at 2 or 24 hours, \(G_1\) is mass of the completely dried samples before putting in water, \(G_2\) is mass of the samples after absorbing water for 2 or 24 hours. The softening coefficient was measured according to equation (2) as follows:

\[
f = \frac{R_2}{R_1} 
\]

where \(f\) is softening coefficient of samples, \(R_1\) is compressive strength of the completely dried samples before putting in water, \(R_2\) is compressive strength of samples whose water content reaches the saturation point.

3. Results and Discussion

3.1. The effect of NaOH on water absorption and softening coefficient of FGD-FA-SS composites

The water absorption and softening coefficient of samples with different mass percentages of NaOH added are presented in figure 1. It can be seen that the addition of NaOH reduces water absorption at 2 hours and 24 hours while it increases softening coefficient of samples, which illustrates that the water resistance of composites is improved by the addition of NaOH. With regard to the water absorption at 2 hours and 24 hours, they initially decrease with the increase of NaOH addition from 0 to 1.5wt% and then basically remain the minimum value of 18.36 and 19.93%, respectively, when the content of NaOH is over 1.5wt%, which decreased by 40.52 and 37.80%, respectively, as compared to samples without NaOH addition. As for the softening coefficient, it exhibits an increasing trend at the beginning stages and then remains mainly unchanged. When the content of NaOH is 1.5%, softening coefficient reaches a maximum value of 0.53 increasing by 51.43%, as compared to blank samples. The alkalinity of FGD-FA-SS composites is improved by the addition of NaOH which decomposes the glass structure of FA and SS and promotes the release of silicon-oxygen bond and aluminum-oxygen bond that trend to react with \(\text{Ca}^{2+}\) and \(\text{SO}_4^{2-}\) ions to produce more hydration products such as ettringite and hydrated calcium silicate. The holes between dihydrate gypsum crystals can be filled with these products resulting in densification of FGD-FA-SS composites. Besides, the products are adhered to the surface of dihydrate gypsum crystals which hinders dissolution of desulfurized gypsum and improve the water resistance of FGD-FA-SS composites.
3.2. The effect of RPP on water absorption and softening coefficient of FGD-FA-SS composites

Figure 2 illustrates the impact of RPP on water absorption and softening coefficient of FGD-FA-SS composites. As shown in the curve graph, the water absorptions at 2 and 24 hours gradually decrease, while softening coefficient gradually increases with RPP from 0 to 5wt%. It is evident that the tendency of descent or increase is sharp when the content of RPP is below 3wt% and the curves of water absorption and softening coefficient both become smooth when the content of RPP is over 3wt%. According to the values of water absorption and softening coefficient in figures 1 and 2, water absorption at 2 and 24 hours and softening coefficient of composites with 3wt% RPP addition are 16.36%, 18.93% and 0.55 slightly better than those of the samples with NaOH addition. The increase of water resistance for samples with RPP addition is chiefly attributed to the improvement of the pore structure which is propitious to reduce the water permeation into FGD-FA-SS composites [12]. Besides, RPP tends to generate polymer film on the surface of dihydrate gypsum crystals which reduces the solubility of gypsum resulting in improvement of water resistance.

3.3. The effect of NaOH and RPP co-doped on water absorption and softening coefficient of FGD-FA-SS composites

The results of water absorption and softening coefficient of FGD-FA-SS composites with NaOH and RPP co-doped are presented in figure 3. As shown in figure 3, water absorptions at 2 hours and 24 hours exhibit a decreasing trend and softening coefficient shows an increasing trend at the beginning stage, while they remain substantially unchanged when the content of NaOH exceeds 1.5wt% (or the content of NaOH exceeds 3wt%). It can be found that water absorptions at 2 hours and 24 hours and softening coefficient of FGD-FA-SS composites with NaOH and RPP co-doped (1.5wt% NaOH and 3wt% RPP) basically reach an optimal value of 12.15%, 13.68% and 0.62 which are better than water resistance of the blank samples remarkably and similar to water resistance of other cementing materials [14-15]. Moreover, NaOH and RPP co-doped have a more positive effect on water absorption and softening coefficient of composites compared to NaOH or RPP addition separately which is mainly attributed to the synergistic effect of NaOH and RPP on FGD-FA-SS composites. It can also be found from Sections
3.1 and 3.2, NaOH and RPP both improve the pore structure and decrease the gypsum solubility in different ways.

![Graph showing water absorption and softening coefficient](image)

**Figure 3.** The water absorption and softening coefficient of samples with different mass percentages of NaOH and RPP co-doped.

3.4. *The SEM analysis*

![SEM micrographs](image)

**Figure 4.** The SEM micrographs of fracture surface for FGD-FA-SS composites with (a) 0wt%, (b) 1.5wt% NaOH, (c) 3wt% RPP, (d) 1.5wt% NaOH and 3wt% RPP added.

The SEM micrographs of the fracture surface for FGD-FA-SS composites are shown in figure 4. It can be seen that the pore contents decrease with the addition of NaOH and more hydration products can be observed on the surface of FA and SS in the samples with NaOH addition which gives rise to the improvement of water resistance (figure 4(a) and (b)). Besides, the samples with RPP addition are denser than those without RPP addition, which is mainly attributed to the improvement of the pore structure.
caused by RPP addition [12]. It can also be observed from figure 4(a) and (d) that the decreasing trend of pore contents is caught sight and the more hydration products are adhering to the surface of FA and SS in the FGD-FA-SS composites with NaOH and RPP addition due to combined effects of NaOH and RPP resulting in the improvement of waterproof performance (discussed in Section 3.3).

4. Conclusion

NaOH could promote the production of more hydration products such as ettringite and hydrated calcium silicate that led to the improvement of water resistance of FGD-FA-SS composites. When the content of NaOH was 1.5wt%, water absorptions at 2 and 24 hours and the softening coefficient reached an optimum value of 18.36%, 19.93%, and 0.53, respectively.

The addition of RPP could remarkably improve the water resistance performance due to the improvement of the pore structure and decrease of the gypsum solubility. Besides, the water absorption at 2 and 24 hours and softening coefficient of composites with 3wt% RPP addition were 16.36%, 18.93% and 0.55 slightly better than those of the samples with 1.5wt% NaOH addition.

The FGD-FA-SS composites with NaOH and RPP co-doped had a better water resistance performance compared to the samples with NaOH, or RPP added separately which was mainly attributed to the synergistic effect of NaOH and RPP on composites.

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