Study on mechanical properties of FGD matrix composites

T W Liu, Z Wang*, G Z Li, G P Shi and X Zhao
School of Material Science and Engineering, University of Jinan, Jinan, China
E-mail: wangzhi@ujn.edu.cn  Tel: +86- 0531-82767636

Abstract. Flue gas desulphurization gypsum (FGD), fly ash (FA) and steel slag (SS) were by-products during the industrial production process, and comprehensive utilization of these by-products could both protect the environment and save resources. The effects of FA and SS on the mechanical properties of FGD and different activating agents on the mechanical properties of FGD matrix composites were studied. The results showed that mechanical properties gradually decreased with the increase of the content of FA and SS which was principally attributed to the poor hydration activity of FA and SS. The flexural strength and compressive strength of FGD matrix composites were significantly improved by adding NaOH, Al$_2$(SO$_4$)$_3$, and compound activating agent respectively and the compound activating agent had a more positive effect than NaOH and Al$_2$(SO$_4$)$_3$.

1. Introduction
In recent years, flue gas desulphurization gypsum (FGD) has attracted an increasing interest of researchers due to its many excellent properties such as high early strength, low density, nontoxicity and low energy consumption [1-3]. Besides, FGD is a kind of industrial waste solid produced in desulfurization of flue gases in power stations and heating plants, and its output is enormous every year in all the world [4]. As one of the most critical cementitious materials, its energy consumption is lower than that of ordinary Portland cement during the production process which results in the decrease of greenhouse gas emissions [5]. Therefore, FGD is a promising material that can be used for the construction industry. However, its application is limited by some shortcomings such as massive water consumption and water absorption [6]. These problems can be solved by adding siliceous materials such as FA and SS into FGD. Moreover, FA that has pozzolanic activity due to the existence of Al$_2$O$_3$ and SiO$_2$ and SS that has cementing action caused by C$_3$S and C$_2$S are also industrial waste solid [7-8].

Nevertheless, the poor activity of FA and SS hinders their application. One of the most effective methods used to improve the hydration activity is additions of activating agents such as sodium hydroxide and sodium silicate [9-10]. Although FGD with FA and SS addition have enormous potential to be a promising material for applications in renewable energy buildings, few pieces of research about mechanical properties of ternary cementitious materials have been reported.

In this paper, the effects of FA and SS on the mechanical properties of FGD and different activating agents on the mechanical properties of FGD matrix composites were studied.

2. Experimental

2.1. Raw materials
FGD and FA were supplied from Shandong Laiwu Power Plant, and SS was supplied from Laiwu Iron and Steel Group. The chemical compositions of these materials were listed in Table 1. The commercially
available powder NaOH (purity≥96.0%) and Al₂(SO₄)₃ (purity≥98.0%) were used as activating agent to improve the hydration rate of SS and FA in this study. A compound activating agent (made up of Portland cement clinker, Al₂(SO₄)₃ and Na₂SiO₃) was also used to stimulate the 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. Sample preparation and test methods

The FGD was calcined at 155 °C for 200 min and placed at room temperature for 7 days before using it to improve its cementitious performance. The FA and SS were ball-milled using a planetary ball milling machine at a speed of 300 rpm for 6 h before the experiment to enhance hydration activity of FA and SS. The proportions of FGD, FA and SS were given in Table 2. The above material mixtures were mixed using a paste mixer at a speed of 140 rpm for 150 s. After milling, the mixtures were cast into a steel mold of size 16 × 4 × 4 cm and demolded after 24 h. The specimens were cured in air at room temperature until the testing days. The compressive and flexural strengths were measured by an electromechanical universal testing machine (CMT5105, China) and the values reported were obtained by the average of six strength tests.

### Table 2. Mixture proportions of samples (wt%).

| Sample | A1 | A2 | A3 | A4 | A5 |
|--------|----|----|----|----|----|
| FGD    | 100| 90 | 80 | 70 | 60 |
| FA     | 0  | 5  | 10 | 15 | 20 |
| SS     | 0  | 5  | 10 | 15 | 20 |

3. Results and Discussion

3.1. The effect of FA and SS addition on mechanical properties of FGD

The flexural strength and compressive strength of FGD matrix composites with different mass percentages of FA and SS added are showed in Figure 1. It can be seen from figure 1 that flexural and compressive strength values of samples after 7 and 28 days show a decreasing trend with the increase of content of FA and SS. When the additions of FA and SS are both 20wt%, the flexural and compressive strength values after 7 days reach a value of 2.12 and 8.76 MPa, respectively, which implies the decline by 34.37 and 31.62%, as compared to blank samples (A1). The drop in mechanical properties is principally attributed to the poor activity of FA and SS which causes the low speed of hydration reaction. Besides, flexural and compressive strength values of samples after 7 days have a steeper trend than those of samples after 28 days. Flexural strength and compressive strength at 28 days reach a value of 2.67 and 10.78 MPa, respectively dropping by 18.10 and 16.17%, as compared to samples without FA and SS. It can be observed that the addition of FA and SS significantly reduces the mechanical properties of FGD after both 7 and 28 days. Therefore, it is essential to improve the poor activity of FA and SS using the addition of activating agents which are propitious to the increase of mechanical properties.
3.2. The effect of NaOH addition on mechanical properties of FGD matrix composites

Figure 2 presents that the flexural strength and compressive strength of FGD matrix composites with NaOH addition (adding 0-2.5wt% NaOH into A5 sample). It can be observed that the flexural strength and compressive strength after 7 and 28 days of FGD matrix composites have mostly the same variation tendency. These mechanical properties are enhanced with the increase of NaOH at the initial stage (0-2.0wt%) and then reach the maximum values of 2.59 MPa, 10.86 MPa, 3.41 MPa and 14.13 MPa when the content of NaOH is 2.0wt% which increase by 22.17%, 23.97%, 27.72%, and 31.08% respectively compared with the samples without NaOH addition. NaOH can improve the basicity of FGD matrix composites and destroys the glass structure of FA and SS resulting in the release of silicon-oxygen bond and aluminum-oxygen bond which can react with Ca$^{2+}$ ions SO$_4^{2-}$ ions to produce more hydration products such as ettringite and hydrated calcium silicate. While continually increasing NaOH from 2.0wt% to 2.5wt%, these mechanical properties exhibit a downward trend which reveals that excessive NaOH addition has an adverse effect on FGD matrix composites.

![Figure 1](image1.png)

**Figure 1.** The flexural strength and compressive strength of FGD matrix composites with different mass percentages of FA and SS added.

![Figure 2](image2.png)

**Figure 2.** The flexural strength and compressive strength of FGD matrix composites with NaOH addition (0-2.5wt%).
3.3. The effect of $\text{Al}_2(\text{SO}_4)_3$ addition on mechanical properties of FGD matrix composites

Figure 3 exhibits the influence of $\text{Al}_2(\text{SO}_4)_3$ addition on flexural strength and compressive strength of FGD matrix composites (adding 0-2.5wt% $\text{Al}_2(\text{SO}_4)_3$ into A5 sample). It is evident that flexural strength and compressive strength after 7 and 28 days gradually increase when the content of $\text{Al}_2(\text{SO}_4)_3$ ranges from 0 to 1.5%. The samples with 1.5wt% $\text{Al}_2(\text{SO}_4)_3$ addition possess the highest values of 2.63, 11.02, 3.48, and 14.56 MPa, which are higher by 24.06, 25.80, 30.34, and 35.06%, respectively, as compared to samples without $\text{Al}_2(\text{SO}_4)_3$ addition. The release of $\text{Al}^{3+}$ ions from $\text{Al}_2(\text{SO}_4)_3$ is the primary factor leading to the improvement of mechanical properties. $\text{Al}(\text{OH})^{2+}$ is generated by the reaction of $\text{Al}^{3+}$ and $\text{OH}^-$ that originates from FGD matrix composites system and then converted into zeolite hydration product through reacting with $\text{Ca}^{2+}$ and $\text{Na}^+$ ions to enhance the mechanical properties of samples. The slight drop in the mechanical properties emerges when the content of $\text{Al}_2(\text{SO}_4)_3$ is over 1.5wt% which illustrates the counterproductive effect of excessive $\text{Al}_2(\text{SO}_4)_3$ addition.

![Figure 3](image.png)

**Figure 3.** The flexural strength and compressive strength of FGD matrix composites with $\text{Al}_2(\text{SO}_4)_3$ addition (0-2.5wt%).

3.4. The effect of compound activating agent addition on mechanical properties of FGD matrix composites

The flexural strength and compressive strength of FGD matrix composites with compound activating agent addition are presented in Figure 4. As indicated in the curve graph, compound activating agent can significantly improve mechanical properties of FGD matrix composites. It can be clearly seen that the flexural compressive strengths after 7 days and 28 days increase gradually from 2.12, 8.76, 2.67, 10.78 MPa to 2.86, 11.94, 3.83, and 15.12 MPa with the increase of compound activating agent addition from 0 to 1.5wt%, which is attributed to the rise of hydration products caused by combined effect of various components of compound activating agent such as Portland cement clinker, $\text{Al}_2(\text{SO}_4)_3$ and $\text{Na}_2\text{SiO}_3$. It can be concluded by calculation that the flexural strength and compressive strength of samples with 1.5wt% compound activating agent added after 7 and 28 days is 34.90, 36.30, 43.46, and 40.26%, respectively, higher than those of samples without activating the added agent [11]. When the content of compound activating agent increase from 1.5 to 2.5wt%, the mechanical properties of samples remain essentially unchanged which discloses that more beneficial effects cannot be produced through adding overmuch compound activating agent into FGD matrix composites. Moreover, comparing compound activating agent with NaOH and $\text{Al}_2(\text{SO}_4)_3$, the activated effect of the former on FGD matrix composites is better than that of the latter two.
Figure 4. The flexural strength and compressive strength of FGD matrix composites with compound-activating agent addition (0-2.5wt%).

3.5. The XRD analysis
XRD patterns of FGD and FGD matrix composites are presented in Figure 5. It can be seen from pattern X that the main hydration product of pure desulphurization gypsum is made up of dihydrate gypsum, while peaks of ettringite emerge in the pattern of the FGD with FA and SS. However, the peak intensity of ettringite is very weak due to the poor activity of FA and SS which causes the low speed of hydration reaction. As demonstrated in the XRD patterns of samples with compound activating agent addition (pattern Z), the peak intensity of ettringite is strengthened compared to the peak intensity of ettringite in the samples without compound activating agent addition. It can be considered that the activation of steel slag and fly ash is stimulated after adding compound activating agent which is propitious to produce hydration products through the reaction between FGD, FA, and SS, resulting in improvement of mechanical properties of FGD matrix composites. Besides, dihydrate gypsum peak intensity of samples with FA and SS (pattern Y and Z) is lower than that of samples with FA and SS addition (pattern X) which also indicates that the reaction between FGD, FA and SS causes the reduction of dihydrate gypsum.

Figure 5. XRD patterns of FGD and FGD matrix composites (X: pure FGD gypsum; Y: FGD with 15wt% FA and 15wt% SS; Z: sample Y with 1.5wt% compound activating agent).
4. Conclusions
In general, the mechanical properties of FGD matrix composites gradually decrease with the increase of the proportion of FA and SS in the composite material system which is principally attributed to low hydration ability of FA and SS in the early stage.

The flexural strength and compressive strength of FGD matrix composites are improved by adding NaOH and Al$_2$(SO$_4$)$_3$ respectively which reveals that NaOH and Al$_2$(SO$_4$)$_3$ have a positive effect on hydration process of FA and SS.

The activated effect of the compound activating agent on FGD matrix composites is higher than that of NaOH and Al$_2$(SO$_4$)$_3$ due to the combined impact of various components of the compound activating agent. When the content of the compound activating agent is 1.5wt%, the mechanical properties of FGD matrix composites reach the maximum values.

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