

EVALUATION OF USING FLY ASH-SLAG-BASED MORTAR AS A MINE BACKFILLING MATERIALS PROPERTIES AND HYDRATION CHARACTERISTICS

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INTRODUCTION

Due to the tight land resources, incineration is considered the best means of domestic waste treatment, not only for the high degree of capacity reduction, which can reach more than 90%, but a large amount of MSWI Fly Ash, a by-product of the incineration process, is considered a hazardous waste due to its high content of heavy metals and organic pollutants (Yang and Ji et al., 2018; Li and Zhang et al., 2020). The heavy metals in MSWI FA cannot be removed and can only be transformed in different forms. Currently, S/S is an economical and widely used technology due to its physical and chemical fixation that can effectively trap toxic substances in MSWI FA in the solidified body (Kan and Shi et al., 2020; Xue and Liu, 2021). In this study, the mechanical properties of GGBS-SS-FGD mortar system and the leaching of heavy metals from mortar under different environments were evaluated by studying the incorporation of MSWI FA, so as to select the optimal amount of MSWI FA to be added to the GGBS-SS-FGD system.

MATERIALS AND METHODS

(1) Raw materials

GGBS, SS and FGD were obtained from Jingtaicheng Environmental Resources Co. Ltd in Hebei province, China. In order to facilitate adequate hydration reactions, the raw materials were dried and ground thoroughly in a ball mill after delivery to the laboratory. The MSWI fly ash was collected from a MSW incineration power plant located in Chengdu, China. The incinerator used in this domestic waste incineration plant is a grate furnace.

(2) Preparation of mortar samples

The designed composition of samples are listed in Table 1. The mortar samples were prepared at a water-to-binder of 0.5 and standard sand-to-binder ratio of 3, and samples were poured into a steel mould (40*40*160mm). All samples were placed in a standard constant temperature and humidity cement curing box (humidity 95% \pm 1%, temperature 20°C \pm 5°C) for 1

days before mould removal. They were then placed in a curing box for curing to the corresponding age.

(3) Heavy metals leaching method

Mix concentrated sulfuric acid and concentrated nitric acid with a mass ratio of 2:1, adjust the pH of the leaching solution to 3.2, and carry out a tumbling and shaking test on the curing body according to the liquid-solid ratio of 10:1, adjusting the rotational speed to 30 \pm 2r/min and shaking for 18h.

Table. 1 The designed composition of samples

Sample number	Binders (g)				Standard sand (g)	Water (ml)
	fly ash	GGBS	SS	FGD		
FBM0	0	306	90	54	1350	225
FBM1	22.5	283.5	90	54	1350	225
FBM2	67.5	238.5	90	54	1350	225
FBM3	135	171	90	54	1350	225

The leaching amount of heavy metals is determined according to GB/T 30810-2014 test methods for leachable ions of heavy metals in mortar. The 10.0g mortar powders with particle size between 0.125 and 0.25mm were selected, which were added to 500 ml deionized water. The pH value of the suspension was titrating to pH 7.0 \pm 0.5 and remaining 2h by the mixed solution (the solution was prepared by mixing solution A and B, solution A: adding 100ml H₂SO₄ to 200 ml deionized water; solution B: adding 50 ml HNO₃ to 100 ml deionized water) while stirring. After filtration, the 500 ml deionized water was added to the residue, and the pH value of the suspension was titrating to pH 3.2 \pm 0.5 then remaining 7h while stirring. The filtrate from the above two steps was collected and diluted to 2L.

The pH dependent leaching test was conducted following EPA 1313. This method was designed to assess the pH leaching behaviour of inorganic

components in terms of equilibrium conditions at different pH values. In this work, 8 suspensions were prepared with pH values at 12、11、10、9、8、6、4 and 2. Each suspension was made of 30g samples and 300ml deionized water in 500ml HDPE vessels. The end-pH value was achieved by adding HNO_3 and NaOH solution.

RESULT AND DISCUSSION

Both the mechanical properties and the leaching of heavy metals from the mortar affect the practical use of fly ash slag base as backfilling material, and for underground backfilling in mining areas, the compressive strength is required to be between 1 and 4 MPa. In order to evaluate the safety performance of the mortar the total amount of leachable heavy metals in the mortar is evaluated. Considering that the backfilling material will not only be in contact with groundwater in practical application, but also the artificial roof may be in contact with acid rain, the leaching of heavy metals from the fly ash slag base under this environments needs to be evaluated. However, the HJ299 test standard only requires an initial pH of 3.2 for the leaching solution, while fly ash slag-based mortar is a strongly alkaline material. In order to evaluate the leaching of heavy metals from fly ash slag-based mortar under extreme pH environments, the mortar was tested for pH dependence.

(1) Mechanical property

After 3 d and 7 d of curing, the compressive strength of all groups with FA added was lower than that of FBM0 (Fig.1), which was due to the dispersed size of FA particles and their own low volcanic ash reactivity, which led to a decrease in the overall hydration reactivity and strength of the system(Liu and Hu et al., 2020; Fan and Wang et al., 2021; Gj and Xma et al., 2022). However, with the extension of the curing time, the release of OH^- from the dissolved FA particles promotes the breakage of $[\text{Si-O-Al}]$ and $[\text{O-Si-O}]$ bonds in GGBS and SS, which accelerates the hydration reaction(Xu and Ni et al., 2019). Thus when after 28 d of maintenance, the compressive strength of FBM2 is 32.62 MPa, which is almost the same as that of FBM0. This phenomenon also indicates that as the reaction proceeds more fly ash particles are dissolved to participate in the hydration reaction. Similar to the compressive strength, after 3 d curing, the flexural strength of all the added FA groups was lower than that of FBM0, but the flexural strength of FBM2 was comparable to that of FBM0 after 28 d curing, and the strength increased by 210.71%, which could reach 4.35 MPa. Similarly, this also indicates that although FA has poor hydration activity by itself, the strength of FA cured body increased significantly with the extension of curing time. The strength of FA cured body increased significantly with the increase of curing time. Therefore, it is considered that the mechanical properties of FA are best at 15% admixture.

(2) Heavy metals leaching \

According to the experimental results of GB/T 30810-2014 as shown in Figure 2.FA leaching of various heavy metals exceeded the limit, when the content of FA in FBM group was lower than 30%, the leaching content of various heavy metals was lower than the limit value in GB 30760-2014; however, when the content of FA was 30%, the leaching content of Zn was 1052ug/L, which exceeded the limit value, and the leaching content of Cd Although it is lower than the limit value of 30ug/L, but it is more dangerous. This is due to the fact that Zn is the most abundant among the various heavy metals in FA, which is still an order of magnitude lower than the leachable concentration of 47014 ug/L of Zn in FA. Although the leached content of Cr was not exceeded in any of the groups, it is noteworthy that the leached concentration of Cr in FB0 was higher when no FA was added, which was likely from SS. In general, the curing body cured the various heavy metals in FA better when the FA addition was less than 30%. A point of interest is that when the leaching method of HJ299 was used for SW, the leaching content of heavy metals in each group was extremely low (Table 2), and none of them exceeded the limit value. This is due to the fact that compared to the GB 30810 leaching method under fixed pH conditions (pH=7 maintained for 3h and pH=3.2 maintained for 3h), the HJ299 leaching method requires a fixed starting pH of 3.2, but the curing body is alkaline, as shown in Table 2, when the end pH of each group at the end of the leaching was in the alkaline range, indicating that probably most of the H^+ was in the cured body. It has been extensively studied that the endpoint pH significantly affects the leaching of heavy metals from the curing body, which will be elaborated in the next section.

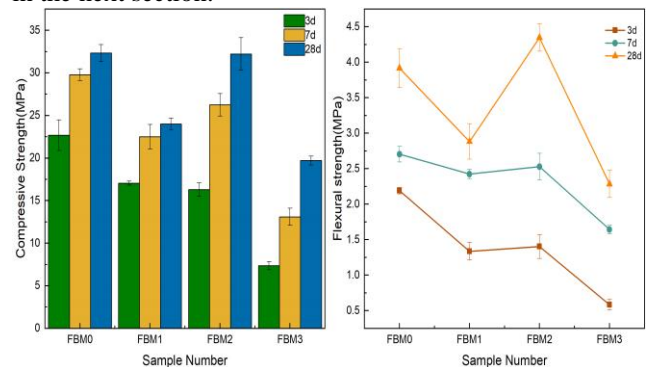


Figure 1. FBM mechanical properties:(a) compressive strength; (b) flexible strength

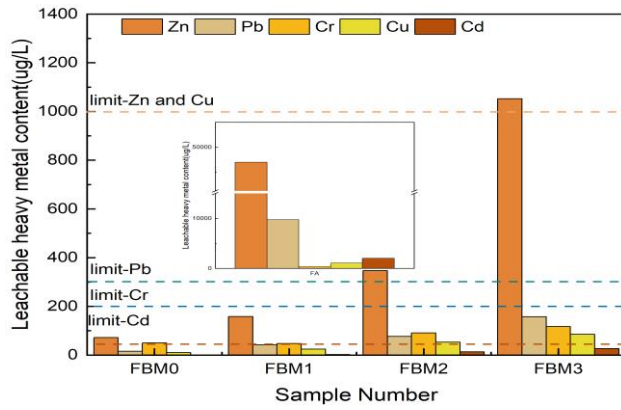


Figure 2. Total leachable heavy metals in FBM
Table. 2 HJ299 test the leaching of heavy metals in FBM

Samples	Zn	Pb	Cd	Cu	Cr	Leaching end
number						point pH
FBM0	NA	NA	NA	NA	0.06	9.71
FBM1	NA	NA	NA	NA	0.03	10.21
FBM2	NA	NA	NA	NA	0.02	10.52
FBM3	0.53	0.07	0.02	0.03	0.09	10.57

In order to investigate the effect of endpoint pH on the leaching of heavy metals and to evaluate the safety and stability of FBM, the leaching of heavy metals was studied in the pH range of 2-12 (Figure 5). In the solidified body, some heavy metals of FA are present in new mineral phases or immobilized by some hydration products, such as ettringite, C-S-H. It is interesting to note that both of these cases occur in a low alkaline environment (pH 8-11 range), so the leaching of various heavy metals is extremely low in the range of 8-11 as shown in Figure 3(Liang and Ysw et al., 2020; Xiang and Feng et al., 2020). Based on the leaching behavior of heavy metals, the heavy metals in the cured bodies can be classified into two categories, the first being amphoteric metals such as Pb, Zn and Cr; the other being Cu and Cd whose leaching concentration increases with decreasing pH. The leaching concentration of Pb in FA shows a V-shaped dependence on pH, and when FA is in a very basic and acidic environment, the leaching concentration of Pb is two orders of magnitude higher than that in a neutral environment. When the curing body is in the pH=12 environment, even FBM3 did not appear Pb leaching, while the leaching of Pb in FA was 10.54 mg/L; when in an acidic environment, at pH=6, the leaching concentration of Pb in all curing bodies can meet the standards of groundwater tertiary water, compared to FA at pH=4 has exceeded the hazardous waste

identification standards (GB5085). The leaching concentration of Pb in the cured body group was two orders of magnitude lower than that of the FA, compared to the FA at pH=4, which already exceeded the limit value of Pb in the hazardous waste identification standard (GB5085). It is believed that the curing body cures Pb extremely well, especially for alkaline environments, mainly because the hydration product of the curing body, ettringite, is stable in alkaline environments, while when in acidic environments, the high presence of H^+ may lead to decomposition of ettringite decalcification, thus reducing the curing efficiency of Pb. The leaching behavior of Zn is similar to that of Pb, both exhibited obvious amphoteric metal leaching characteristics, and although the concentration of Zn in the original FA was high, for the cured body group, the leaching concentration of Zn was lower than the limits of GB16889 and GB5085 even in a very acidic environment with pH=2. Same as the leaching behavior of Pb in the cured body in a very alkaline environment, the leaching concentration of Zn remained undetected at pH=12. The leaching concentrations of Cr in the cured bodies in Figure 3(e) were low overall, but the difference between the leaching concentrations of Cr in the cured bodies and the original MSWI FA for each group at pH=2 was not significant due to the fact that Cr was mainly from SS. The leaching behavior of Cd and Cu was typical of the cationic leaching pattern, i.e., the leaching concentration increased with decreasing pH. At pH=4, the leaching concentrations of Cd in FBM1 and FBM2 were below the detection limit. According to the available studies on the mechanism of Cd curing is mainly in the form of $Cd(OH)_2$ precipitation on the surface of C-S-H gel, but the reaction of C-S-H gels with H^+ in an acidic environment generates non-gel or soluble material, which in turn leads to the decomposition of C-S-H, and the increased porosity of the cured body also increases the risk of Cd leaching(Fei and Jian et al., 2021). As shown in Fig. 3(d), the S/S efficiency of the solidified body for Cu is so high that the leaching concentration of Cu in FBM1 is only 0.39 mg/L, which is lower than the standard for tertiary groundwater (1 mg/L), even in a pH=2 extremely acidic environment.

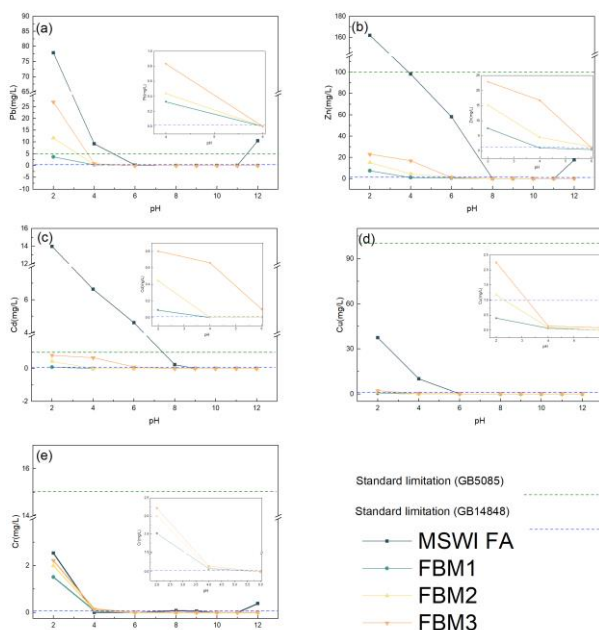


Figure 3. FBM pH dependence test results

CONCLUSION

According to the mechanical properties and the leaching of heavy metals, when the addition of fly ash is 15%, not only the compressive strength of fly ash slag-based mortar can reach the standard of OPC 32.5 cement, but also the content of heavy metals in the test method according to HJ299 are not exceeded, at this time fly ash slag-based mortars no longer belongs to hazardous waste. Moreover, in the pH dependence test of the mortars, the leaching of heavy metals of mortars under alkaline conditions was significantly reduced after the curing stabilization treatment, which is due to the stabilization of the hydration products in the curing body under alkaline conditions. In addition to this, fly ash slag-based mortars has a stronger resistance to acid attack compared to original fly ash, which substantially reduces the leaching of heavy metals under acidic conditions.

Therefore, it is concluded that the GGBS-SS-FGD system has an excellent curing and stabilizing effect on heavy metals in FA, and the mechanical properties of the mortars can also meet the standard, and it is considered that the fly ash slag-based mortar has the possibility of practical application as backfill material in mine extraction areas.

ACKNOWLEDGEMENT

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