Study on properties development of the composite cementitious system with milled fly ash of ash dam

Jianfeng Zhang¹*, Yan Shi¹, Jixiao Wang² and Xingdong Lv ¹

¹Changjiang River Scientific Research Institute of Changjiang Water Resources Commission, Wuhan, 430010, China
²Huadian Jinsha river upstream hydropower development co. LTD, Chengdu, 610041, China

*Corresponding author’s e-mail: 349478952@qq.com

Abstract. The performance development of the composite cementitious material system with fly ash and milled fly ash of ash dam were investigated. The results show that, compared with fly ash, the milled fly ash of ash dam with special morphology has not significant morphology effect and microaggregate effect at the initial hydration stage. Under the same conditions, the composite cementitious system of milled fly ash of ash dam has a larger water demand ratio and a longer setting time, and the early strength of concrete is relatively low, but the later strength increases rapidly, which is basically equivalent to the strength of concrete with fly ash. After mixing phosphorous slag powder, the water demand ratio of composite cementing system of the milled fly ash of ash dam is obviously reduced, and the setting time is further prolonged, but the strength of early cementing sand can be improved.

1. Introduction
A large amount of fly ash from power plants is deposited and built in ash storage sites without being utilized, which is called ash dam. It has no practical use, wastes space and pollutes the environment. Fly ash of ash dam has a long accumulation time and low grade, and is rarely used in engineering practice[1]. With the vigorous development of China’s water resources and hydropower engineering construction, the demand for hydraulic concrete mineral admixture is increasing day by day[2]. At present, the southwest of China is in the peak period of hydropower station construction, and many large hydropower projects will be started successively. Due to the shortage of local large thermal power plants, the fly ash resources are limited, and the transport distance is generally long, which leads to the high price of fly ash. However, the local sources of fly ash of ash dam ash industrial waste is rich, if it can partially or completely replace the fly ash, it will not only significantly reduce the project cost. It also has great economic and social benefits to improve the efficiency of resource utilization and promote the construction of ecological civilization.

A large number of studies have shown that[3-5], on the one hand the volcanic ash materials of phosphorus slag, volcanic ash and limestone powder into cement cementing system can improve the particle gradation of cementing materials, fill the cement particles, effectively block the internal bleeding channel, and reduce the liquid flow in the slurry. On the other hand, due to its pozzolanic activity, it can react with Ca(OH)₂ to form cementing substances with stable properties and improve the performance of concrete. In order to better study the hydration characteristics of the milled ash of ash dam as an auxiliary cementitious material, in this paper, the performance development law of
composite cementitious system of the milled ash of ash dam, fly ash and phosphorus slag is compared and studied, which provides guidance for the application of ash dam in hydropower engineering.

2. Testing

2.1. Materials and mix ratio
For this study, moderate heat Portland cement of grade 42.5(P-MH 42.5), conforming to Chinese National Standard GB200-2017 was used. (Specific gravity-3170kg/m³, specific surface area-336m²/kg, normal consistency-25.6%, initial and final setting time-245min and 351min respectively, 3d, 7d and 28d compressive strength of cement mortar-24.9MPa, 30.3MPa and 47.0MPa respectively). Fly ash is grade II fly ash (F) of xuanwei power plant and pangang power plant and grade II milled fly ash (Fb) of ash dam.(Screen residue(0.045mm)-12.5, 14.7 and 14.3, water demand ratio-102, 97 and 102, activity index-69,70 and 71 respectively.

Phosphorus slag grinding powder (P) is controlled according to the specific surface area of 300m²/kg~350m²/kg (P351) and 350m²/kg ~ 450m²/kg (P426). (water demand ratio-98 and 100, and the 28d activity index-92 and 93 respectively). It is mixed with selected fly ash, and the mixing mass ratio is: phosphorus slag powder: fly ash = 4:6, 5:5, 6:4. Content of PF material (phosphorous slag powder and fly ash mixture) and PFb material (phosphorous slag powder and ash dam ground fly ash mixture) : moderate heat Portland cement is tested by 30%, 55% and 65%. Sand is ISO standard sand, mixing water is tap water, the water/cement ratio of mortar is 0.5, the binding material/sand ratio is 1:3. The chemical composition of cementitious material is shown in table 1 and the mixing proportion of composite cementitious materials is shown in table 2.

Table 1. Chemical compositions (by mass) of binders (%)

| Binder                  | CaO  | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO  | SO₃  | Na₂Oeq | Lost  |
|-------------------------|------|------|-------|-------|------|------|--------|-------|
| Cement                  | 61.39| 20.31| 4.18  | 5.12  | 3.34 | 2.38 | 0.45   | 1.54  |
| Fly ash (Xuanwei)       | 3.24 | 58.93| 21.59 | 9.67  | 1.25 | 0.13 | 0.77   | 0.95  |
| Fly ash (Pangang)       | 3.04 | 51.41| 24.80 | 6.50  | 3.13 | 0.36 | 2.34   | 5.17  |
| Fly ash dam milled ash  | 1.70 | 51.03| 29.62 | 5.68  | 1.91 | 0.36 | 1.95   | 4.64  |
| Phosphorus slag (351)   | 48.44| 37.33| 2.87  | 1.33  | 2.98 | 0.90 | 0.52   | 0.47  |
| Phosphorus slag (426)   | 48.60| 37.64| 2.90  | 1.27  | 2.98 | 0.89 | 0.52   | 0.47  |

Table 2. Mix proportion (by mass) of complex binders

| Sample | Cement | Fly ash | milled fly ash of ash dam | Phosphorus slag |
|--------|--------|---------|---------------------------|-----------------|
|        |        | Xuanwei| Pangang | ash dam | P351  | P426  |
| F1     | 100    | 0      | 0      | 0       | 0     | 0     |
| F2     | 70     | 30     | 0      | 0       | 0     | 0     |
| F3     | 70     | 0      | 30     | 0       | 0     | 0     |
| F4     | 70     | 0      | 0      | 30      | 0     | 0     |
| F5     | 70     | 18     | 0      | 0       | 12    | 0     |
| F6     | 70     | 18     | 0      | 0       | 0     | 12    |
| F7     | 70     | 0      | 18     | 0       | 0     | 12    |
| F8     | 70     | 0      | 0      | 18      | 0     | 12    |
| F9     | 35     | 39     | 0      | 0       | 0     | 26    |
| F10    | 35     | 0      | 39     | 0       | 0     | 26    |
| F11    | 35     | 0      | 0      | 39      | 0     | 26    |
2.2. Specimen preparation and method
Cuboid specimens with dimensions of 40mm×40mm×160mm were maintained to the specified age. Compressive strength at different ages were tested by reference to GB/T 17671-1999. Jsm-5610lv scanning electron microscope produced by JEOL company of Japan was used to observe the micro morphology of fly ash, milled fly ash of ash dam and phosphorus slag.

3. Results and discussion

3.1. Cement net paste properties
The physical performance test results of cement paste with different kinds of fly ash composite cementitious materials are shown in table 3. It can be seen from table 3, that the addition of fly ash and phosphorous slag powder to cement slurry has a certain impact on the normal consistency, water demand ratio and setting time. Compared with fly ash of different varieties, arranged in order of the water requirement of normal consistency and water demand ratio of composite cementitious materials, the sequence are ground II milled fly ash of ash dam, pangang grade II fly ash and xuanwei grade II fly ash. The setting time of cementitious materials are pangang grade II fly ash, ground II milled fly ash of ash dam and xuanwei grade II fly ash in turn. In the mixture, with the increase of the proportion of phosphorus slag powder, the water requirement of normal consistency of cement slurry decreases, the water demand ratio decreases, and the setting time increases. When the fly ash variety and content are constant, the water requirement of normal consistency, water demand ratio and initial setting time of P351 and P426 are basically the same, but the final setting time of cement slurry mixed with P426 phosphorous slag powder is prolonged. There indicates that has no significant influence on the performance of cement net slurry, when the specific surface area of phosphorus slag powder increases from 351 m²/kg to 426 m²/kg.

The main factors affecting the water demand ratio of composite cementitious materials include fineness, carbon content, microbead content and morphology. The more spherical particles in fly ash, the fineness of the thinner, the greater the lubrication effect, the less the water demand ratio, and the better the water reduction effect[6,7]. The particle morphology of different types of fly ash and phosphorus slag is shown in figure 1. There are a lot of regular spherical particles in ground II milled fly ash of ash dam. However, compared with other kinds of fly ash, the surface of the particles is rough, some of the particles are observed to have concave holes, and contain a lot of irregular shapes of impurities. Due to the fly ash particles are extremely fine, it is difficult to test the content of microbeads, and there is no mature test method for reference. The vitreous and microbeads content of fly ash is calculated by statistical methods based on SEM images. The statistical results of the content of microbeads of various fly ash varieties are listed in table 4. It can be seen that xuanwei grade II fly ash contains more vitreous and microbeads, so its water demand ratio is small.

Fly ash and phosphorus slag will prolong the setting time of concrete. When phosphorus slag powder is added, it will have a more significant impact on the setting time of cement. This is because containing phosphorus, fluorine and other elements, especially the phosphorus. The dissolution of phosphorus, together with Ca²⁺ and OH⁻, generates fluorohydroxyapatite and calcium phosphate, which cover the surface of C₃A, thus inhibiting its hydration and leading to delayed coagulation[8,9].

| Sample | Normal consistency (%) | Water demand ratio (%) | Setting time (min) | Volume stability   |
|--------|------------------------|------------------------|-------------------|-------------------|
|        |                        |                        | Initial setting   | Final set         |
| F1     | 28.2                   | 100                    | 245               | 319               | Up to standard    |
| F2     | 28.6                   | 102                    | 264               | 350               | Up to standard    |
| F3     | 31.5                   | 113                    | 343               | 500               | Up to standard    |
| F4     | 33.2                   | 116                    | 318               | 433               | Up to standard    |
F5 26.8 95 258 308 Up to standard
F6 27.0 96 290 352 Up to standard
F7 29.0 103 417 513 Up to standard
F8 30.7 106 354 459 Up to standard
F9 26.6 94 421 606 Up to standard
F10 26.8 95 472 654 Up to standard

Table 4. Content of vitreous and microsphere in fly ash of different varieties (%)

| Sample                  | Xuanwei class II fly ash | Pangang class II fly ash | Fly ash dam milled ash |
|-------------------------|--------------------------|--------------------------|------------------------|
| Vitreous                | 80.3                     | 73.2                     | 70.3                   |
| Microsphere             | 67.3                     | 57.5                     | 46.6                   |

Figure 1. Morphologies of different kinds of fly ash

3.2. Cement mortar properties

The compressive strength test results of the compound cementitious material with fly ash and phosphorous slag powder are shown in figure 2. As can be seen from figure 2, when fly ash and phosphorous slag are used instead of cement, the compressive strength of cement mortar will be reduced compared with that of pure cement cement sand and the early strength varies greatly. Thanks to the volcanic ash reaction continued, the late strength gap gradually narrowed. The compressive strength of mortar mixed with pangang grade II fly ash are the highest and the strength of mortar mixed with pangang grade II milled fly ash of ash dam are the lowest. With the increase of the content of phosphorus slag powder and fly ash, the compressive strength of composite cementitious system decreases gradually. With the extension of age, the compressive strength increases gradually. The compressive strength of cement mortar mixed with PF and PFb is higher than that of fly ash alone, and the compressive strength increases with the proportion of phosphorus slag powder in the mixture. When the content is low (<50%), there is little difference in the compressive strength of cement mortar mixed with P351 and P426. When the content is high and the age is ≥28d, especially when the age is 90d, the compressive strength of cement mortar mixed with P426 is significantly higher than that of cement mortar mixed with P351, which is because the larger the specific surface area of phosphorus slag powder is, the higher the activity will be, especially the larger the content is, the easier to exert the activity effect at age. Under the same conditions, the pangang grade II milled fly ash of ash dam and phosphorus slag powder are mixed,which reduces the difference in strength between the cement cement sand and other kinds of fly ash. It indicates that the mixed phosphorus slag powder and fly ash can improve the strength of composite cementitious system in the early stage. While in the later stage of hydration, the hydration degree of fly ash is significantly lower than that of phosphorus slag, so the strength of the composite cementitious system mixed fly ash and phosphorus slag powder is gradually higher than that of the single fly ash.
4. Conclusion

(1) Compared with grade II fly ash, the water demand ratio of the composite cementitious material with milled fly ash of ash dam increases and the setting time is prolonged, which is caused by the particle morphology, fineness and chemical composition of fly ash.

(2) The early strength of mortar mixed with milled fly ash of ash dam is low, but the later strength increases rapidly, which is basically equivalent to the strength of mortar mixed with fly ash. When the content is low, there is no obvious difference between the strength of mortar mixed with milled fly ash of ash dam and grade II fly ash.

(3) After mixing with milled fly ash of ash dam and phosphorous slag powder, the water demand ratio can be effectively reduced and the setting time can be further prolonged. However, it can improve the strength of composite cementitious system in the early stage, while in the later stage of hydration, the strength is also higher than that of fly ash alone.

Acknowledgements

The authors are grateful to the support from the National Key R & D Program of China (2016YFB0303601), National Natural Science Foundation of China (51779019, 51479011 and 51509020) and the central non-profit scientific research fund for institutes under granted (No. CKSF2017052/CL).

References

[1] Y. Shi, Y.C. Wang, H.Q. Yang. (2009) Contrast study on performance of fly ash dam milled ash and other high quality fly ash. Concrete, 237:64-66.

[2] H.Q. Yang, W.W. Li. (2005) Research and application of hydraulic concrete. China Waterpower Press, Beijing.

[3] X. Li, Y. Shi, L.Z. Li. (2009) Compressive Strength development of Complex Binders Containing Tuff Powder. JOURNAL OF BUILDING MATERIALS, 20(3):438-441.

[4] E. Ercan, K. Adnan, D. Gulnaz. (2011) Strength enhancement of Eskisehir tuff ashlars in Turkey. Construction and Building Materials, 25(7):3014-3019.

[5] C. Messaouda, B. Abderrahim, S. Kameil. (2013) Concrete mix design containing calcareous tuffs as a partial sand substitution. Construction and Building Materials, 27(47):318-423.

[6] H.Q. Yang, Y. Dong, S.H. Zhou. (2018) Mineral admixtures for hydraulic concrete. China Waterpower Press, Beijing.

[7] Y.J. Xue, D.X. Xuan, Y. Zeng. (2006) Effect of Fly Ash Fineness on Performance of Cementitious Matter/Sand in Cement. COAL ASH CHINA, 18(2):10-11.

[8] Y.C. Wang, Y. Su, S.H. Zhou. (2011) Cement mixture and concrete admixture. Chemical Industry Press, Beijing.

[9] D.X. Li, J.L. Shen. (2001) The influence of fast-setting/early-strength agent on high phosphorous slag content cement. Cement and Concrete Research, 31(1):19-24.