The deteriorated microstructure characteristics of fly ash doped cementitious materials by dissolution

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Abstract: The microstructure differentiation of fly ash doped cementitious materials between before and after dissolution was observed by XRD and MIP to analyze the microstructural deterioration characteristics of different samples. Results showed that there were great changes in hydration products, cement clinker and fly ash particles after dissolution. Pore structure evolution during dissolution indicated that the effect of C-S-H decalcification on pore structure was not negligible and the traditional definition between the harmful pore and the harmless pore was not applicable.

1. Introduction

In modern civil and hydraulic engineering, some buildings such as water diversion tunnel, dam panel, sluice, underwater construction, etc., are in long-term contact with water, of which cementitious materials are prone to dissolution damage. Relevant investigation results show that the occurrence frequency and damage degree of concrete dissolution is second only to the cracking of concrete among the main durability problems of hydraulic structures in China [1]. Moreover, the leaching of environment-related substances, especially some toxic substances, has also attracted attention with the increasing awareness of environmental protection and the extensive use of various mineral admixtures. For example, Wolfram Müllauer et al. [2] and A. Vollpracht et al. [3] have studied the precipitation of trace elements of Portland cement paste and fly ash or slag doped concrete from the point of view of environmental safety. Therefore, it is necessary to pay sufficient attention to the dissolution of cement-based materials in the need of engineering safety or environmental safety. In the early 20 centuries, Soviet scientists showed concern for the dissolution phenomenon of concrete. In recent decades, relevant researches have made some achievements [4]. With further development of science and technology making micro-scale research possible, the study on dissolution has gradually shifted from macroscopic performance to microstructure. The microstructure of cementitious materials paste is one of the most important factors affecting the mechanical properties and durability [5-7], as well as the focus of studying the material deterioration mechanism. In recent years, Pan Feng et al. [8] established a 3D model of phase stability, microstructure and properties during leaching. N. Bossa et al. [9] combined with micro- and nano-CT techniques to study the pore structure characteristics during dissolution process and obtained a complete three-dimensional pore network. Early similar studies mainly focused on the microstructure of pure cement specimens (without mineral admixtures), however, the microstruc-
ture of concrete becomes more complex due to the incorporation of various mineral admixtures. For this reason, some researchers have carried out some preliminary studies. Xiang, Yan Peiyu et al. [10] and F.H. Han, et al [11] studied the effect of dissolution on microstructure of fly ash-cement materials. Li YJ Tang, et al [12] analyzed the influences of water-binder ratio and slag content on microstructures of slag-cement pastes in the process of calcium leaching. Q.T. Phung et al. [13] studied the microstructures and transmission characteristics of cementitious materials with limestone during dissolution process.

At present, there are still few reports concerning how the solid phase and pore structures of paste evolve during dissolution, and there is a great controversy about the pore structure deterioration. Mainguy [14] indicated that the increase of porosity was due to the dissolution of calcium hydroxide (CH) and the effect of hydrated calcium silicate (C-S-H) was negligible. However, others [9, 13] argued that the increase in pore by C-S-H resulted in the increased connectivity of pore structure, and the polymerization effect of C-S-H by decalcification would cause micro-cracks, increasing the permeability to promote dissolution. In addition, there is also a great deal of controversy over the order of dissolution of hydrated products [8, 15-19].

In this paper, the deteriorated microstructure characteristics of fly ash-cement materials with different dosages by dissolution have been studied by XRD and MIP. The different characteristics of solid phase (involving hydration products, clinker and fly ash particles) before and after dissolution and the evolution of pore structures during dissolution have been obtained. The results will provide experimental base for clarifying the microstructure deterioration mechanism of fly ash-cement hydrating and hardening paste under dissolution.

2. Material and Methods

2.1. Materials

The 42.5 moderate-heat Portland cement and the first-grade fly ash used in the experiment are produced by Xinjiang Tianshan Cement Joint-Stock Co., Ltd. and Yunnan Qujing Fangyuan Environmental Protection Building Material Co., Ltd., respectively. The chemical compositions of cementitious materials are shown in Table 1.

| Composition | CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | SO₃ | *R₂O | LOI |
|-------------|-----|------|-------|-------|-----|-----|------|-----|
| Cement      | 62.50 | 25.60 | 0.87  | 1.20  | 3.49 | 2.42 | 0.36 | 1.26 |
| Fly ash     | 3.20  | 53.44 | 24.51 | 11.11 | 1.14 | 0.73 | 1.09 | 2.24 |

* R₂O is the equivalent of alkali content, R₂O=Na₂O+0.658K₂O

2.2. Preparation of specimens

A cube specimen of 40 mm*40 mm*40 mm was molded by a cement paste mixer according to the mix proportion shown in Table 2, and then was transferred to a standard curing tank for curing (temperature 20±1℃, relative humidity greater than 90%) After curing for 1d, the specimen was demoulded, and then cured to 28d under the same environment. The four surfaces of the specimens were sealed with paraffin (two of the surfaces as shown in Figure 1 (a)) prior to the accelerated dissolution test to ensure that the dissolution test was carried out in one-dimension state.

2.3. Tests

The NH₄NO₃ solution was used to simulate the accelerated dissolution of the specimen by ambient water [20], and the concentration of NH₄NO₃ was 3mol/L. Each container with 2L NH₄NO₃ solution and 15 specimens was sealed with film to reduce the evaporation of water (as shown in Figure 1 (b)). The whole experiment process was under the environment with temperature 20±1℃, and the solution was replaced every two weeks. As the dissolution time increased to the corresponding age (7d, 28d, 90d, 180d), specimens were broken and soaked in ethanol to discontinue its dissolution and hydration.
Table 2. Mix proportion of cementitious materials

| Specimen | Water to binder(w/b) | Composition (%) |
|----------|----------------------|-----------------|
|          |                      | Cement | Fly ash |
| C        | 0.35                 | 100    | 0      |
| F20%     |                      | 80     | 20     |
| F35%     |                      | 65     | 35     |
| F50%     |                      | 50     | 50     |
| F65%     |                      | 35     | 65     |

The hydration product compositions of the cementitious material paste before and after dissolution were analyzed by D8 Advance X-ray diffractometer (CuKa, 40KV, 40mA, the angle reproducibility of 0.001° produced by Bruker AXS company) over a scanning range of 5°~60° in 2θ scale. The step increment (or length) applied was 0.0194303°.

The pore size distribution and porosity of the different pastes were determined by using the AUTOPORE IV 9520 mercury intrusion porosimeter (MIP) (the maximum mercury intrusion pressure of 414MPa, the applicable pore size in the range of 3nm~1000μm). In order to study the deterioration law of the paste structure of the dissolution process, the samples of different ages were uniformly taken from the paste within 5mm of the outermost dissolved area.

3. Results and discussion

3.1. Hydration product change

X-ray diffraction (XRD) is a technique for phase analysis using X-ray diffraction effects in crystalline phase. The change of cement clinker and crystalline hydration products during hydration or dissolution can be identified by XRD. The XRD spectrums of the pure cement sample and the fly ash-doped sample are shown in Fig. 2, where C and CF denote the spectrums of the specimens before dissolution; RF-90d and D-90d refer to the spectrums of dissolved area of specimens for 90d dissolution and C-90d and CF-90d refer to the spectrums of sound area of specimens for 90d dissolution.

Figure 2. The XRD spectrums of the pure cement sample and the fly ash-doped sample
As shown in Fig. 2(A), there were a large amount of calcium hydroxide (CH), partially unhydrated cement clinker phases (C₂S and C₃S) and a small amount of gypsum (G) and ettringite (AFt) in the pure cement sample before dissolution. After dissolution for 90d, the diffraction peaks of calcium hydroxide weakened and the diffraction peaks of C₂S disappeared in the dissolved area, while the diffraction peaks of calcium hydroxide and C₂S almost stayed unchanged in the sound area. The results implied that the dissolution of calcium hydroxide and C₂S had occurred due to dissolution effect. The difference in the diffraction peaks of the gypsum and C₃S between the XRD spectrums of C and C-90d indicated that the interior of the specimen was undergoing slow hydration when the outer layer of the specimen was undergoing dissolution. The comparison results of CF and CF-90d (shown in Fig. 2(B)) showed that significant hydration also occurred in the fly ash-doped specimen, consuming a lot of C₂S and C₃S and some calcium hydroxide, and resulting in the generation of ettringite, monosulfoaluminate (AFm) and other crystal products. But in dissolved area, the amount of calcium hydroxide extremely decreased, and C₃S disappeared; ettringite and monosulfoaluminate were also absent.

The above analysis showed that dissolution was a slow process for the whole specimen. The interior of the specimen was undergoing slow hydration when the outer layer of the specimen was undergoing dissolution. It meant that the hydration degree of the paste in the dissolved area was not uniform along the direction of dissolution, the type and the quantity of the hydration products were also not the same, resulting in a gradient dissolution phenomenon at a certain degree in the dissolved area.

3.2. Pore structure deterioration
Pore is a non-solid phase microstructure element of hardened cement paste and an important component of hardened cement paste, of which the parameters, such as porosity, pore size distribution and pore morphology, are all some of important structural features of hardened cement paste. Using MIP method, the evolution of pore structure to deterioration direction due to dissolution effect has been observed in the study. In the Fig.3 (A) ~ (E) (corresponding to specimens with 0, 20%, 35%, 50%, 65% fly ash), the pore size distribution of the hardened paste is reflected by the differential curve of the cumulative mercury intrusion volume which is the total pore volume corresponding to a certain pore size. The corresponding pore size of the peak of the curve is called the most probable pore size, which is the pore size with the largest volume content in paste.
Figure 3. The differential curve of the cumulative mercury intrusion volume vs pore size diameter of various samples with multiple ages

From the beginning of dissolution to 7d, there was a phenomenon that the most probable pore size was shifting to the larger pore size of the total volume of pores near the most probable pore size was increasing, indicating that the original pore of the paste was in the stage of expansion at this time, and the body of the dissolution was mainly the hydration product and cement clinker on the original pore wall; that is to say that environmental solution was gradually going to the internal paste along the original pore during this period, and the expansion of pore was caused by the dissolution of the hydrated product and cement clinker around the original pore. During the period of 28d~90d, a large number of pores of 3nm~5nm were produced in the pure cement paste, pores with diameter less than 10nm were also produced in the 20% fly ash sample (shown in Fig. 3 B-28d) and there was a similar phenomenon in other fly ash samples, indicating that the body of dissolution was not limited to the solid phase around the original pores, and the dissolution effect further developed upon the inner solid phase area, resulting in the formation of a large number of new small pores. After 90d of dissolution, as the depth of dissolution was further deepened, solid phase was dissipating in a large amount, resulting in the continuous expansion of original pores, the generation of new small pores and the development of the whole pore structure toward deterioration. However, during the period of dissolution of 90d, it was still found that there was a decrease in the pore volume of certain pores in addition to an expansion of original pores and an increase in the number of new pores; but the phenomenon was not just the result of dissolution of paste since there was no correspondingly increasing volume of pores near the left side at some size ranges in the figure, while there was a significant increase in the vicinity of its right side. The results showed that there was also an effect by hydration on pore structure during the period since
the corresponding pores were filled by hydration products due to the continuing hydration of the cement clinker and the secondary hydration with fly ash. In spite of the hydration effect, the effort of dissolution on the pore structure of the sample is more obvious, leading to the deteriorated development of pore structure as a whole. When the dissolution continued to 180 d, the pores structure further deteriorated, the peak position of curve continued to move to left side, the pores within 100nm~1000nm increased significantly, and the pores of 3nm~10nm almost disappeared. It was deduced that a number of pores formed by a large number of soluble hydration products led to the reduction of distance among pores in the later dissolution stage, some larger pores were easily generated by a perforation action between pores when the material further dissolved, so that all pores of 3 nm to 10 nm were expanded into pores of larger than 10 nm; the same reason was to the phenomenon of other samples. However, there was an abnormal phenomenon in the sample with 60% fly ash with a large number of 3nm~10nm pores. Its analysis indicated that perhaps, in the later dissolution stage, the dissolved phases were mainly composed of hydrated calcium silicate and others which were smaller and more difficult to dissolve than calcium hydroxide; correspondingly, the resulting pores were much smaller, leading to the new pores by expansion still relatively small, so it could be observed in the figure that the pores below 5nm have disappeared at 90 d, then they occurred again at 180 d.

The pores were classified combining the above two classification methods as below 5nm, 5nm~20nm, 20nm~50nm, 50nm~100nm, 100nm~200nm, above 200nm and the distribution of the pore size after division was shown in Fig. 3 (a) ~ (e). The most probable pore size range of all samples mainly distributed at 5nm ~ 50nm, with little change at various ages; however, it could be seen from the previous analysis that the samples have deteriorated seriously in the later stage of dissolution, so it hinted that the increasing number of pores and the increasing connectivity between pores were the main manifestations of the deterioration of the pore structure. It was also shown that in the case of the paste subjecting to dissolution, the circumscription between the harmful pore and the harmless pore was no longer obvious; at this time, although pore size was still an important index to pore structure, its impact on the pore structure was no longer dominant due to the increase in the number of pores and the connectivity, so that pores of below 100 nm, which were previously defined as the less harmful or harmless pores, may also be detrimental to the structure of the paste by dissolution.

4. Conclusion
The effect of dissolution on microstructure of fly ash doped cementitious materials was investigated. Based on the combined XRD and MIP data presented, the following conclusions were drawn:

1. There was a gradient dissolution phenomenon at a certain degree in the dissolved area due to the hydration difference of dissolved area along the direction of dissolution. The hydration products in the fly ash samples with multiple percentages were changed greatly by dissolution.

2. The analysis of pore structure showed that not considering surface dissolution, the dissolution occurred firstly in the original pore wall area, and then gradually reached into the solid phase region. The body of the increased pore volume by the dissolution was not only present as the individual small pore, but also as part of the pore enlarged by expansion and merger of the original pore. It implied that the effect of a large amount of C-S-H decalcification on pore structure was not negligible and the circumscription between the harmful pore and the harmless pore was no longer obvious. Considering the change of porosity, the 20% fly ash sample compared with all specimens had the best anti-dissolution property in the long-term dissolution process.

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