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Influence of slag content and water-binder ratio on leaching behavior of cement pastes

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HIGHLIGHTS

- Slice specimens with slag-cement paste were designed to carry out the calcium leaching experiment.
- Influences of slag content and water-binder ratio on the leaching resistance of cement pastes were investigated.
- The slag-cement pastes with the optimum leaching resistance were obtained.

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ABSTRACT

In order to obtain quickly the influences of blast furnace slag and water-binder ratio on the leaching behavior of cement-based material and its corrosion resistance in water environments, an accelerated calcium leaching experiment on a slice specimen with slag-cement pastes in 6 M NH_4 Cl solution was carried out. Using the saturation-drying weighing method, X-ray diffraction (XRD) and the scanning electron microscope (SEM/EDS) measurement, the influences of water-binder ratio and slag content on the porosity, phase composition, microstructure morphology and Calcium-Silicon ratio of slag-cement pastes in the process of calcium leaching were analyzed. Results show that, compared to cement pastes without slag, the slag-cement paste with the appropriate slag content has a low rate of microstructure deterioration and a good leaching resistance. The optimum slag contents in slag-cement pastes are respectively 40% and 50% corresponding to the low and high water-binder ratio. The porosity, Calcium-Silicon ratio and microstructure morphology of slag-cement pastes exhibit small change in the process of accelerating leaching, and this indicates that the slag-cement pastes with the optimum slag content can provide the best performance of calcium leaching resistance in the soft-water environment.

1. Introduction

Concrete structures such as dams, ports, bridges and pipelines, located in rivers, lakes and other water environments, are easily corroded by soft water, causing the material durability deterioration and structural performance reduction of concrete [1–3]. Under the attack of water environment, the dissolved calcium ions in pore solution from the cement hydration products $Ca(OH)_2$ and C-S-H gel in concrete flow into the water due to the great gradient of the calcium ion concentration, and this phenomenon, which is called the calcium leaching, leads to the reduction of the calcium content in concrete, the decrease of alkalinity of the pore solution and the increase of porosity of concrete [4–7]. Calcium leaching also causes the reduction of concrete strength, the increase of concrete permeability, and weakens the protective effects of concrete on steel bar [6,5]. Water attack is one of the important environmental factors leading to the durability degradation of concrete structures [1,8]. Both the blast furnace slag mixed in concrete and the reduction in water-binder ratio can improve its microstructures, also increase the calcium leaching resistance of concrete in water environment [9–15].

Recently, some advanced studies on the influence of slag on the hydration characteristics and the microstructure evolution of cement-based materials have been conducted [16–20]. Lumley [16] studied the influences of curing age, slag content and water-binder ratio on the hydration degree of slag in the slag-cement pastes, and obtained that, under the curing ages of 28 days and 2 years, the hydration degrees of slag in the slag-cement pastes with the water-binder ratio 0.4∼0.6 and the slag contents 30%∼60% are 40% and 75%, respectively. Taylor [17] carried out the SEM-XRD analysis of the microstructure evolutions of slag-cement pastes cured in water for 20 years, and results show that, the $Ca(OH)_2$ content has a gradual decrease, while the hydration

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degree of slag in the matrix increases slowly. Zhen [20] examined the influences of slag content on the hydration characteristics of cement paste, and observed that, at high water-binder ratio, the slag-cement pastes with 30% slag content has the optimum microstructure with the minimum porosity and the most compact structure after the hydration.

The blast furnace slag can effectively improve the microstructure of cement-based materials, and enhance its calcium leaching resistance in water environment [21–23]. Presently, some researches have been carried out to investigate the influences of slag on the calcium leaching behavior of cement-based materials subjected to the attack of the pure water or accelerated solutions [19,22,24–26]. Jain et al. [22] investigated the changes of porosity and calcium hydroxide content in plain and modified cement pastes in pure water with leaching time by using weighing and thermogravimetric method respectively, and obtained that the compactness and calcium hydroxide content in the cement pastes decrease with the leaching time, in which the decrease of compactness, or the increment of porosity is mainly caused by the leaching of calcium hydroxide. Liu [19] utilized Scanning Electron Microscope(SEM) to observe the microstructure morphology of leached slag-cement pastes with water-binder ratio caused by the attack of flowing deionized water, and the evolution characteristics of its microstructure have been revealed in the long-term process of leaching. Due to very slow natural calcium leaching, some accelerated leaching tests on cement-based materials have been conducted to investigate the effects of calcium leaching on the materials' performance [27–31]. Yang et al. [25] performed the accelerated leaching experiment to study the influence of calcium leaching on the mechanical properties of cement paste, such as hardness and compressive strength, by using 6 M ammonium chloride solution, and the relationship between mechanical properties and leaching duration has been observed to forecast the compressive strength of the leached cement-based materials on the long term. Wan [26] investigated experimentally the equilibrium curve of Ca in 6 M ammonium nitrate solution to clarify the accelerated leaching mechanism in cement-based materials, and observed from the comparison between the equilibrium curves of Ca in 6 M ammonium nitrate solution and in water that they have similar three-staged equilibrium curves, and their dissolving and leaching mechanisms are also similar.

The current studies have revealed the influence mechanism of slag on the hydration characteristics and the initial microstructure of cement-based materials, analyzed the influence of slag on the calcium leaching resistance of cement-based materials in different water environment. But there have been few studies on the optimum mix proportion of slag-cement materials with the best leaching resistance. The optimum mix proportion has an important guiding significance for the design of concrete structures with high resistance to calcium leaching. In order to obtain the optimum mix proportion of slag-cement materials for improving their leaching resistance, the influences of water-binder ratio and slag content on the microstructure evolution of cement-based material and its corrosion resistance in the process of calcium leaching need to be further studied. In this paper, some slice specimens with the slag-cement pastes, which can reduce the influence of calcium ion transport, was designed to carry out an accelerated calcium leaching experiment by using 6 M NH_4Cl solution, and the influence of slag content and water-binder ratio on the leaching process of the slice specimens were investigated to obtain the optimum leaching resistance. The porosity, material composition, microstructure morphology and Calcium-Silicon ratio of the slag-cement pastes in the process of calcium leaching were tested by using the saturation-drying weighing method, scanning electron microscope (SEM/EDS) and X-ray diffraction(XRD), and by comparing the tested results from the compositional differences at different leaching times, for each slag content and water-binder ratio, some information on the influence of slag content and water-binder ratio on the calcium leaching process were obtained to further ascertain the slag-cement materials with the optimum leaching resistance.

2. Experiments

2.1. Materials

The cement used in this study is the 52.5-grade Portland cement, having chemical composition as listed in Table 1. The density of cement is 3150 kg/m^3, with specific surface area of 369.6 m^2/kg. The initial and final setting time are 72 min and 290 min respectively, and its normal compression strength and flexural strength for 28 days curing are 60.5 MPa and 8.7 MPa respectively. S95-grade blast furnace slag powder with a density of 2.9 g/m^3 and a specific surface area of 435m^2/kg was used as an additive mixture. Clean tap water and pure water were used to mix the slag-cement pastes, and prepare the ammonium chloride solution respectively. Table 2 lists the mixture ratio of slag-cement pastes with different water-binder ratio.

Ammonium chloride reagent with a solubility of 37.2 g/100 ml at room temperature was used to prepare the accelerated leaching solution with the concentration of 6 M. Similar to the accelerated leaching mechanism of ammonium nitrate solution, the ammonium chloride solution is also a chemical acceleration technique, which can be used to establish the long term leaching in cement-based materials [24,25,31]. The principle of chemically accelerated leaching on cement-based materials is to promote reaction between calcium hydroxide and ammonium chloride in the leachant solution, forming gaseous ammonia and calcium chloride, which is highly soluble in water (see Eq. (1)) [25].

$$Ca(OH)_2 + 2NH_4Cl = Ca^{2+} + 2OH^- + 2H^+ + 2NH_3(\uparrow) + 2Cl^- = CaCl_2 + 2NH_3(\uparrow) + 2H_2O \quad (1)$$

2.2. Sample preparation and test methods

According to the mixtures listed in Table 2, One hundred slice specimens with water-binder ratio of three and size 10 mm × 10 mm × 2 mm were prepared, as shown in Fig. 1, and then placed in the curing box at environmental temperature of (20 ± 1) °C and relative humidity greater than 95% for curing of 28-and 90-days respectively. Next, a total of 12 groups were made, with each group containing two 2.5-grams slices in separate nylon-fiber-mesh bags, and then put into 12 water boxes filled with 5 L of 6 mol/L ammonium chloride solution, as shown in Fig. 2.

For the slice specimens with slag-cement pastes subjected to the accelerated leaching, its porosity, pore size and distribution, the changes of which can be used to characterize the leaching process, have very great changes in a relatively short leaching time, but the change of the porosity can be more directly to reflect the leaching degree of cement-based materials than the pore size and distribution. Thus, in this study, the saturation-drying weighing method [22,32], which is a simple and suitable for engineering applications, is used to measure the average porosity to characterize the influences of blast furnace slag and water-binder ratio on the leaching resistance of slag-cement materials. The unleached slice specimens, as well as those leached in ammonium chloride solution for 1, 3, 5, 7, 9, 12, or/and 15 days, were subjected to porosity measurements in accordance with the procedure described in the existing document [22]. The SEM observation and XRD phase analysis for the slice specimen immersed into the solution for different leaching time were respectively carried out