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Study on chloride binding capability of coal gangue based cementitious materials

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HIGHLIGHTS

- Coal gangue will become a promising supplementary cementitious materials.
- The chloride binding isotherm of all specimens can be described by Freundlich equation.
- The chloride binding capability of slag is stronger than that of coal gangue.
- The addition of coal gangue can change the chemically and physically bound chloride capability.
- The chloride binding capability of coal gangue was dependent on the content of alumina, CH and SiO_2.

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ABSTRACT

The addition of supplementary cementitious materials containing Al_2O_3 can improve the chloride binding capability of hardened cement paste to varying degrees, thereby enhancing the durability of reinforced concrete structures. This work was designed to investigate the high-aluminum coal gangue based cementitious materials chloride binding capability, including coal gangue content, coal gangue-slag combined addition and coal gangue calcination temperature. The phase composition and Friedel's salt contents in the specimens were evaluated by XRD and TG-DTG analysis. The results showed that the specimens chloride binding isotherms could be described by Freundlich equation. The coal gangue optimal content was between 20% and 30% and the maximum content was 40%. The chloride binding capability of slag was stronger than that of coal gangue, which promoted the formation of Friedel's salt. In the content range of this study, the chloride binding capability of coal gangue specimens increased at first and then decreased with the increase of the molar ratios of Ca/Si and Si/Al. When the coal gangue-slag composite was added, the chloride binding capability increased with the increase of the mole ratios of Ca/Si and Si/Al, presenting a positive linear relationship.

1. Introduction

The intrusion of chloride ions can cause corrosion of steel reinforcement in reinforced concrete, which leads to loss of structural integrity and decrease service performance [1]. However, the reinforced corrosion is not proportional to the diffusion of total chloride ions in the reinforced concrete structure, and thus the bound chloride does not pose a hazard to the steel reinforcement [2–4]. Therefore, increasing the chloride binding capability of cementitious materials is another important method to improve reinforced concrete structures durability [5].

A large number of studies have shown that the addition of auxiliary cementitious materials containing Al_2O_3 can improve the chloride binding capability of hardened cement paste in varying degree [6–8]. Coal gangue (CG), one of the largest industrial solid wastes in China, contains high Al_2O_3 [9–11], whose crystalline mineral phase is decomposed into SiO2 and Al2O3 components in a high temperature and has strong pozzolanic activities [12,13]. In the decomposition products, the contents of Si_2O_3 and Al_2O_3 are high and the CaO contents is low, which can be complementary to the high CaO content in ordinary Portland cement(OPC) and improve the components and properties of cementitious materials. At present, coal gangue is mainly used for the cement production, road construction, sintered and non-sintered bricks etc. [14]. Compared with OPC, calcined coal gangue has a lower carbon footprint, which makes coal gangue as the most promising industrial

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by-product instead of fly ash, slag and metakaolin etc. [15]. This paper studies on the chloride binding capability of coal gangue, which not only has the solid waste recycling effect, but also provides the theoretical and experimental basis for coal gangue widely replacing cement as the auxiliary cementitious material.

Many scholars [16–18] had developed extensive research on the chloride binding capability of supplementary cementitious materials. However, the main achievements are concentrated on that of common supplementary cementitious materials, such as silica fume (Al_2O_3 0–1%), slag (Al_2O_3 10–20%), fly ash (Al_2O_3 17–35%) and metakaolin (Al_2O_3 30–45%). The addition of silica fume is unfavorable to chloride binding [19,20]. The chloride binding capability firstly increases and then decreases with the increase of the slag content. When the content of slag is 40%, the chloride binding capabilities the strongest [21]. And when the content reaches 70%, the chloride binding capability is still higher than that of pure cement paste [22]. The chloride binding capability increases with the increase of the fly ash content (0%–50%) [23], however, there are also studies finding that the optimal content of fly ash is 25% [24]. Dousti et al. [8] found that the high Al_2O_3 content in metakaolin significantly increased Fridell's salt content in the mixture, and an addition of 40% metakaolin achieved the maximum effect of the chloride binding capability [25]. In general, the Al_2O_3 phases (AFm, AFt, and Al_2O_3 hydration products, etc.) in these supplementary cementitious materials participate in formation of Friedel's salts to improve the chloride binding capability. However, different kinds of supplementary cementitious materials have different chemical compositions, physical properties and spatial structures, and there are different contributions and mechanisms of the hardened cement paste on chloride binding. So far there has been little research into the effect of high-aluminum coal gangue on chloride binding, and the mechanism of chloride binding has not been discussed.

This work was designed to investigate the effect of high-aluminum coal gangue substituting cement on chloride binding of hardened cement paste, and further explore the chloride binding mechanism of coal gangue. The effects of the coal gangue content (10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt%), the coal gangue and slag composite addition (50%) and the calcination temperature of coal gangue(500 °C, 600 °C, 700 °C, 800 °C and 900 °C) on chloride binding were studied. The chloride was all from the external leaching solution, the there was no chloride in the internal solution. The chloride-containing cementitious material phase structure was characterized by X-ray diffractometer (XRD). The contents of the Friedel's salt and $Ca(OH)_2$ was determined by thermogravimetric analysis. It provides the theoretical basis for the following extensive applications of coal gangue based cementitious materials.

2. Materials and methods

2.1. Materials

High-aluminum coal gangue produced in Shanxi, China was selected. After being crushed by the jaw crusher, the small ball of coal gangue was ground to a surface area of 400 m^2/kg, and then the coal gangue was calcined in the constant temperatures of 500 °C, 600 °C, 700 °C, 800 °C and 900 °C for 2 h and rapidly cooled to room temperature. The grade S95 ground granulated slag (SG) with the fineness of 450 m^2/kg supplied by Hebei Iron and Steel Company was chosen. P.O.42.5 OPC was selected as clinker. Analytical reagents of $AgNO_3$ and NaCl were adopted, and mixing water used distilled water.

The main chemical composition of the cementitious materials were analyzed by X-fluorescence spectrometry (XRF) as shown in Table 1. By the X-ray diffraction (XRD) observation of the original and different temperature calcined coal gangue mineral composition, shown in Fig. 1. The main mineral compositions of coal gangue are kaolinite, muscovite and quartz, with the increase of temperature, the kaolinite diffraction peak decreases and the quartz diffraction peak increases. The kaolinite diffraction peak basically disappears after calcination except in 500 °C. The hydration modulus HM = $(CaO + MgO + Al_2O_3)/SiO_2$ and the alkalinity coefficient $K_b = (CaO + MgO)/(SiO_2 + Al_2O_3)$ of high-aluminum coal gangue is 0.64 and 0.01, respectively, which means it is an acid volcanic ash material; the hydration modulus HM and alkalinity coefficient K_b of slag are 1.94 and 1.10, respectively, which means it is an alkaline volcanic ash material. The content of $SiO_2 + Al_2O_3$ in calcined coal gangue exceeds 90%, and the CaO content in slag is much higher than that of coal gangue.

2.2. Specimen preparation and curing

The specimens were prepared with the cementitious material and distilled water, and the W/B ratio was 0.35. The mixture proportions of paste are shown in Table 2. Coal gangue was calcined in the temperature of 700 °C, and 100% OPC as a controlled specimen. The effect of coal gangue calcination temperature on chloride binding were studied, the content of coal gangue was 30% and no slag was added. The fresh paste was poured into 40 mm × 40 mm × 40 mm cube test mode, covered with thin polythene sheets and left under ambient laboratory conditions for a period of 24 h, the specimens were demoulded and cured under 20 ± 2 °C saturated lime water conservation 28d. The specimens were removed surface, crushed and sieved to collect particle size 0.3–2.5 mm, next, the particulate specimens were vacuum dried for three days in a desiccator containing the silica gel to remove most of the water. After this, the dried specimens were stored in a desiccator with 11% relative humidity kept by saturated LiCl solution to least 7 days.

2.3. Measurement

2.3.1. Test methods and procedures

Take 25 g (accurate to 0.001 g) dry particle specimens into the 150 ml plastic bottle, then filled into 100 ml of NaCl solution saturated with $Ca(OH)_2$. The NaCl solution had seven different concentrations of 0.1, 0.3, 0.5, 0.7, 1.0, 2.0 and 3.0 M. After this, the bottles were sealed and stored for 5 weeks at room temperature for equilibrium. Determination by Moire method: potassium chromate as an indicator, chloride ion concentration was analyzed by means of potentiometric titration using 0.01 M $AgNO_3$.

Chloride binding test used isothermal adsorption [26], Immersion in particle specimens with chloride solution until reaching equilibrium between the external solution and the pore solution, the reduction in chloride concentration of the host solution is attributed to chlorides being bound by cementitious materials. The bound chloride content can be estimated according to the following formula:

$$C_b = 35.453 \times V \times (C_t - C_f)/W_d \quad (1)$$

Where:

C_b is the amount of bound chloride in mg Cl/g of the specimen

V is the volume of the external solution in mL

C_i is the initial chloride concentration of the external solution in mol/L

C_f is the free chloride concentration at equilibrium of the external solution in mol/L

W_d is the dry mass of the specimen in g.