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Macro- and micro- characteristics of cement binders containing high volume fly ash subject to electrochemical accelerated leaching

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HIGHLIGHTS

- Performances of HVFA binders subjected to accelerated electrochemical leaching both at macro- and micro- levels.
- C–S–H structure characterization of HVFA binders subjected to leaching through FT-IR, ^{29}Si NMR, and SEM/EDX techniques.
- An appropriate fly ash replacement content of HVFA concrete in leaching environment is suggested.

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ABSTRACT

Although high volume fly ash (HVFA) concrete has shown benefits for mass concrete such as dams, the calcium leaching in these hydraulic structures becomes a concern. This paper presents a study on leaching behavior of HVFA concrete on both macroscopic and microscopic scales. The fly ash was added to replace cement at weight ratios ranging from 30% to 70%. Two curing ages, 28 days and 90 days, were tested. An accelerated electrochemical leaching test was developed to investigate leaching characteristics of HVFA mixtures. Leaching calcium contents, compressive strengths and pore structures were examined. Microstructural changes of HVFA concretes after leaching tests were analyzed through FT-IR, ^{29}Si NMR and SEM/EDX techniques. It was found that addition of fly ash into cement could effectively enhance the leaching resistance of cement based materials, but the contents of fly ash should be limited not to exceed 50% of cementitious materials. Fly ash replacement ranging from 40% to 60% produced optimal pore structure that is beneficial to leaching resistance. The fly ash addition also increased condensation polymerization of C–S–H and increased Q^1/Q^2 ratio, leading to a more stable and durable C–S–H gel structure.

1. Introduction

High volume fly ash (HVFA) concrete has been widely used since Canadian Centre for Mineral and Energy Technology (CANMET) had conducted the research between the 1980 s to the 1990 s [1–4]. HVFA concrete is considered as a concrete in which the cementitious binder consists of at least 50% fly ash. For more than two decades, numerous studies and applications have demonstrated its success in various fields, mostly in mass concrete, such as dams, piers, and docks [5–7]. The advantages of using fly ash in concrete as the partial replacement of cement includes improved workability, reduced hydration heat, and reduced construction cost [5]. The high volume replacement of cement by fly ash in mass concrete has been proven effective in controlling cracking caused by heat of hydration at early ages [5,8]. Although the advantages of using high volume fly ash in mass concrete are obvious in hydraulic structure applications, such as in dams and piers construction, the resistance of high volume fly ash concrete to leaching in an aquatic service environment becomes a concern. Water may dissolve alkali and calcium hydroxide, and decompose hydrated silicate and aluminate phases. Reference to the equilibria, for practical purposes, the ultimate residue will consist essentially of hydrous forms of silica, alumina and iron oxide, with all the CaO being leached out. After this stage, the hardened cement paste is totally disintegrated [9–14].

Leaching of calcium ions due to physical–chemical reactions is one of typical deterioration mechanisms for cement based materials [15,16]. The dominant hydrated products of cement based

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materials, such as CH and C–S–H, are sensitive to calcium leaching, with the CH being the least stable [14]. Leaching processes of CH and C–S–H are governed by Eqs. (1), (2):

$$Ca(OH)_2 \iff Ca^{2+} + 2OH^- \tag{1}$$

$$C{-}S{-}H \iff Ca^{2+} + OH^- + SiO_2 \tag{2}$$

Study by Heukamp et al. revealed that C–S–H matrix was highly plastically deformable, and exhibited poor intrinsic cohesion with lower Ca/Si as the consequence of calcium leaching [17]. The loss of calcium ions also reduced pH values of hardened paste pore solution, and caused changes of Ca/Si in C–S–H, leading to significant transformation of C–S–H structure [18,19]. Feldman et al. carried out a leaching test through putting cement paste slides (0.64 mm) into distilled water, and found that the paste expanded initially and then shrank [20]. They considered that the shrinkage was attributed to loss of interlayer calcium ions or Ca–O layer calcium ions in C–S–H. The leaching of calcium from CH and C–S–H led to higher porosity and lower strength, and consequently reduced serviceability of concrete structures. The addition of fly ash makes concrete more sensitive to leaching deterioration. Therefore for hydraulic structures using fly ash concrete, Chinese building codes specifies a limit on the fly ash content for different applications. For structure concrete, the maximum fly ash content shall not exceed 30% of cementitious materials. It is 35% for arch dam concrete, 60% for arch dam with roller compact concrete (RCC), 40–50% for gravity dam concrete, and 60–65% for gravity dam using RCC (DL/T 5055-2007, in China) [21]. These limits are mainly determined based on project experience, and lack of systematic study.

Previous studies on leaching characteristics of concrete are mainly focused on macroscopic properties including changes of calcium concentration, pore structures, and compressive strengths of concrete without supplementary cementitious materials [22–25]. This paper is to present a study on leaching characteristics of high volume fly ash concrete from both macroscopic and microscopic points of view. The purpose is to determine the appropriate content of fly ash in HVFA concrete when subject to the leaching environment. A series of blended cement pastes mixed with fly ash (30–70%) were investigated. The specimens were subjected to accelerated leaching tests through an electrochemical method. The content of leaching calcium ions, compressive strength, and pore structure of mixtures with and without leaching tests were measured to evaluate the effect of fly ash on leaching resistance of cementitious materials mixed with different percentage of fly ash. Furthermore, Fourier transformed infrared (FT-IR) analysis, Nuclear Magnetic Resonance (^{29}Si NMR) method, and Scanning Electron Microscope accompanying Energy Dispersive X-ray (SEM/EDX) techniques were employed to investigate the microstructural evolution of blended cement mixtures with high volume fly ash under leaching condition. These results could help understand the leaching mechanism in LVFA concrete and provide a scientific base for determining the limit content of fly ash in mass concrete subjected to leaching.

2. Materials and methods

2.1. Materials and mixture proportion

ASTM Type I cement and low-calcium fly ash were used in this study. The chemical compositions of cement and fly ash are listed in Table 1 and the mixture proportions are shown in Table 2. Water to cementitious ratio (W/CM) was kept constant of 0.35, and the fly ash content varied at 0, 30%, 40%, 50%, 60% and 70%. To reach a constant slump of 200 mm for each mixture, polycarboxylate superplasticizer was used at different ratio. In order to eliminate the influence of impurity from water on leaching test, the deionized water was employed in concrete mixing. All mixtures have been measured by leached Ca^{2+} contents, compressive strength, and absorption test. Only mixtures with fly ash of 0, 30%, 50% and 70% were carried out by N_2 absorption, FT-IR and ^{29}Si NMR test. SEM/EDX was experimented on the mixtures with fly ash of 0 and 50%.

In order to investigate the mechanical properties and microstructural characteristics of mixtures with high volume fly ash, cubic paste specimens of 70.7 × 70.7 × 70.7 mm were cast in steel molds. After 24 h initial curing at a temperature of 20 °C ± 1 °C, they were then demoulded and further cured in standard curing room at a temperature of 20 °C ± 1 °C and a relative humidity of 90%.

Every mixture consisted of 24 cubes, which divided into two groups (every group had 12 cubes), one for leaching tests and one for hydration reference. In each group, two curing ages were selected, 28 days and 90 days, to study the curing effect on leaching. After 28 days or 90 days curing in standard curing room, one group of six specimens were subject to accelerated leaching test while the other group specimens were immersed in saturated lime solution as control. All leaching tests were conducted at a temperature of 20 °C ± 1 °C and the relative humidity of 50% ± 5%.

2.2. Electrochemical accelerated leaching test

The electrochemical accelerated leaching test apparatus used in this work is shown in Fig. 1. The copper mesh (anode) placed in specimen and the stainless steel plate (cathode) which immersed in water was connected to a DC power supply to provide a potential for accelerating the leaching procedure. The voltage of accelerating test maintained 60 V. Before accelerated leaching test, the specimens were treated. After cured at 28 days or 90 days, each of 6 specimens of leaching test group was connected with wires together via the copper wire mesh to a DC power supply in parallel. The copper mesh was sealed by insulated adhesive plaster and epoxy resin. Deionized water was employed in the leaching test. The control test specimens were moved into saturated $Ca(OH)_2$ solution for continued curing until the predetermined age.

With the leaching test continued, the concentration of the solution in the chamber increased, leading to decreasing of leaching rate. In order to simulate the accelerated leaching procedure effectively, the deionized water was replaced by fresh water at regular intervals. The water replacement regular interval was determined by the calcium ions (Ca^{2+}) concentration of the solution. Considering the solubility of $Ca(OH)_2$, the size of the specimen, and the volume of deionized water, the water replacement regular intervals were determined as follows. For the specimens curing 28 days, the replacement interval was set with 3 days for the first two weeks and 6 days for the rest. For the specimens curing 90 days, the deionized water replacement interval was set with 3 days also for the first two weeks and 12 days for the rest. During the water replacement, the residual water containing dissolved substances was collected for further investigation. To examine the effect of curing age on HVFA mixtures, the paste specimens with curing 28 days were subjected to accelerated leaching test till 90 days, and the ones with curing 90 days were subjected to accelerated leaching test till 360 days.

2.3. Chemical component analysis of leachate and mechanical properties

The calcium leaching was characterized by the content of Ca^{2+}, and the compressive strength was also investigated with and without accelerated leaching tests. At every water replacement interval, the residual of leachate was collected by washing the chamber and specimens. The residual was put into oven to dry and its chemical composition was determined by X-ray fluorescence (XRF). At last, the content of Ca^{2+} was calculated and characterized by per volume of specimen (mg/cm^3). The compressive strengths of leached specimens were measured at the end of the accelerated leaching tests and the control specimens were measured at the same curing age.

Table 1
Chemical composition of cement and fly ash.

Materials	CaO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	SO_3	MgO
Cement	64.00	19.60	4.23	3.89	0.14	0.72	2.84	2.74
Fly ash	1.61	58.00	32.50	3.22	0.41	1.71	0.33	0.53

Table 2
Mixture proportions.

No.	Cement (%)	FA (%)	W/CM	SP (%)	Slump (mm)
P0	100	0	0.35	0.60	185
P30	70	30	0.35	0.50	195
P40	60	40	0.35	0.50	205
P50	50	50	0.35	0.50	215
P60	40	60	0.35	0.40	205
P70	30	70	0.35	0.40	220

CM: cementitious materials (including cement and fly ash).
SP: polycarboxylate superplasticizer, per mass of cementitious materials.