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Effect of fly ash content on the leaching resistance of shotcrete

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Introduction: To investigate the influence of fly ash (FA) content on the leaching resistance of shotcrete, this study adopted FA replacement ratios as the main variables (0%, 15%, 20%, 25%).
Methods: Shotcrete specimens were prepared using the wet-mix spraying method and subjected to accelerated leaching tests in a 6 mol/L ammonium chloride solution. Systematic analyses of compressive strength, porosity, leaching depth, and calcium ion leaching amount were conducted to examine the effect of FA content on the leaching resistance of shotcrete. Microstructural evolution was also analyzed using scanning electron microscopy (SEM).
Results: The results indicate that the incorporation of FA significantly enhances the leaching resistance of shotcrete. An appropriate amount of FA promotes the formation of additional C–S–H gel through pozzolanic reactions at later stages, improving concrete density and inhibiting calcium ion migration as well as the advancement of the leaching front. With a 20% FA content, shotcrete exhibited optimal leaching resistance: after 90 days of leaching, the compressive strength loss rate was 34.13%, porosity increased by only 3.09%, leaching depth reached 22.09 mm, and the total calcium ion leaching was 3.7 mol/L. The synergistic effect of the pozzolanic reaction and the micro-aggregate effect of FA optimizes the pore structure and reduces the content of soluble calcium phases, thereby enhancing the chemical erosion resistance of concrete.
Discussion: The results demonstrate that reactive components in FA can react with calcium hydroxide from cement hydration to form more stable calcium silicate hydrate, significantly delaying the leaching process of shotcrete. At a 20% replacement ratio, leaching damage is effectively suppressed while mechanical performance is maintained. This study provides theoretical and technical support for mix design and engineering application of shotcrete in erosive environments.

KEYWORDS

fly ash, leaching depth, leaching resistance, mechanical properties, porosity, shotcrete

1 Introduction

Shotcrete is a specialized construction material applied by mechanically spraying concrete or mortar at high velocity onto rock surfaces or formwork. It offers advantages such as rapid construction, strong bonding, short initial setting time, and adaptability to complex geological conditions, making it widely used in tunnel linings, slope protection, underground caverns, and hydraulic structures (Banthia, 2019). However, during service, shotcrete is often exposed to harsh environments—such as humidity, high salinity, and extreme pH levels—and is highly susceptible to leaching damage (Galan et al., 2019;

Kaufmann et al., 2021). During cement hydration, products such as calcium hydroxide (CH), calcium silicate hydrate (C–S–H), and ettringite (AFt) are formed (Wang et al., 2025). When tunnel shotcrete is in long-term contact with groundwater, calcium ions from these hydration products continuously leach out under concentration gradients until equilibrium is reached (Tong et al., 2024b). In such calcium-leaching environments, the microstructure of C–S–H gel is severely affected, leading to a decline in the physical and mechanical properties of concrete (Liu et al., 2024). Therefore, improving the durability of shotcrete and exploring methods to enhance its erosion resistance in leaching environments are of great practical importance for engineering applications.

As one of the main components of shotcrete, cement production generates a significant amount of carbon dioxide (CO_2) (Teara et al., 2019), which has considerable environmental impacts. In the context of global efforts to address climate change and promote sustainable development, reducing carbon emissions during the production and application of building materials, and enhancing resource recycling efficiency, have become central issues in industry development. In this process, the use of industrial solid waste to partially replace cement can not only directly reduce cement consumption and production costs but also serves as a key method for promoting a circular economy. FA, a by-product of industrial production, poses potential threats to land resources and the environment due to its large-scale stockpiling. Because of its wide availability, low cost, and benefits in terms of both environmental and performance improvement (Amran et al., 2021), FA is used as a mineral admixture in concrete. Its application can effectively reduce cement consumption, enhance the utilization of waste resources, lower engineering costs, and align with the core principles of green building and low-carbon development (Tamanna et al., 2023). Despite its clear environmental and economic advantages, the long-term durability of FA-blended concrete—especially shotcrete with its unique placement process—and its performance evolution in harsh environments are critical factors determining its reliable large-scale application. This study prepares shotcrete with varying FA contents to examine its physical and mechanical properties after leaching, and analyzes the influence of FA on the leaching resistance of shotcrete.

Numerous studies have been conducted on the performance deterioration of concrete following calcium leaching. Choi and Yang (2013) found that the pore volume of concrete increases with leaching progression. Nguyen et al. (2007) indicated a strong coupling relationship between calcium leaching and the mechanical behavior of concrete, where both strength and stiffness degrade as leaching develops. X-ray diffraction (XRD) analysis of leached concrete by Kargari et al. (2024) showed that peak intensities decrease with longer leaching time, indicating reduced crystallinity of the crystal structure due to the loss of calcium-rich compounds. Choi et al. (2014) performed compressive and flexural tests on leached concrete members, reporting that leaching-induced deterioration leads to a reduction in compressive strength and a transition from brittle to ductile failure behavior during the degradation process. Using an accelerated leaching method with ammonium nitrate, Carde and François (1997) investigated the physical and mechanical properties of leached cement paste. Their study demonstrated that the ratio of degraded area to total area correlates linearly with both strength loss and porosity increase, concluding that the dissolution of CH is a key parameter controlling strength reduction and porosity growth. Zhang et al. (2023) studied the fracture properties of concrete under calcium leaching, observing declines in fracture toughness, elastic modulus, and tensile strength with prolonged leaching time. Leached concrete exhibited faster crack propagation and greater susceptibility to cracking compared to unleached concrete. Di et al. (2023) examined the coupled effect of calcium leaching and wet–dry cycles on the Vickers hardness and pore structure of hardened cement paste. Their findings indicate that calcium leaching primarily increases the porosity of pores larger than 200 nm through the dissolution of calcium hydroxide, while also raising the porosity of pores ranging from 7 to 50 nm by removing calcium from C–S–H gel. From the aforementioned studies, it is evident that the mechanical properties and porosity of concrete change after leaching. In addition, leaching depth and calcium ion leaching amount can also serve as evaluation indicators for concrete leaching (Cheng et al., 2011; Choi and Yang, 2013; Liu et al., 2025; Xia et al., 2025).

Existing studies have shown that the incorporation of FA can improve the physical and mechanical properties of concrete and effectively mitigate performance degradation caused by leaching. Wu et al. (2022) conducted experimental research on the mechanical properties of shotcrete with different FA contents. The results indicated that the 28-day compressive, flexural, and tensile properties of shotcrete gradually decreased as the FA content increased. To avoid excessive strength reduction and ensure structural safety, the FA content should be controlled within a certain range in practical construction. Liang et al. (2024) investigated the influence of FA, silica fume, and slag powder on the calcium leaching resistance of porous cement-stabilized macadam. The results demonstrated that mineral admixtures can accelerate the cement hydration reaction, consume CH to form more stable hydration products, and increase the density of the cementitious matrix, thereby stabilizing calcium ions in the hydration products during the leaching process. Cai et al. (2016) reported that adding FA to cement can effectively enhance the leaching resistance of cement-based materials. However, the FA content should not exceed 50% of the total mass of the cementitious materials. Tong et al. (2024a) found that FA-blended shotcrete exhibited increases of 28.8% in compressive strength and 60% in tensile strength after 28 days of curing. Moreover, FA contributed to a reduction in calcium ion dissolution under long-term curing conditions.

In summary, although domestic and international scholars have conducted extensive research on the leaching mechanisms and influencing factors of concrete under different chemical media and environmental conditions, and have confirmed the improvement effect of incorporating FA, a key limitation remains in the existing studies: most conclusions regarding the influence on leaching performance are based on standard cast-and-vibrated concrete specimens. However, shotcrete differs fundamentally in construction technology. It is formed by high-velocity impact and often contains accelerators, resulting in a more heterogeneous microstructure, higher porosity, and potentially more microcracks (Shalaby et al., 2025). These unique structural characteristics arising from the construction process may lead to significant differences between shotcrete and ordinary cast concrete in terms of physical and mechanical properties as well

TABLE 1 Physical and mechanical properties of cement.

Density (g/cm^3)	Specific surface area (m^2/kg)	Standard consistency (%)	STableility (mm)	Setting time (min)		Flexural strength (MPa)		Compressive strength (MPa)	
				Initial setting	Final setting	3d	28d	3d	28d
3.06	346	28.1	1.0	182	257	6.5	8.6	34.4	57.3

TABLE 2 Chemical composition of cement.

Chemical composition	Al_2O_3	SiO_2	Na_2O	Fe_2O_3	SO_3	CaO	MgO
Content (%)	5.42	21.46	0.38	4.56	0.89	65.51	1.16

as degradation patterns under leaching environments. Systematic research addressing these differences is still insufficient.

This study will prepare shotcrete specimens with different FA contents using the wet-mix spraying method and systematically investigate their durability under calcium leaching conditions. Specimens with varying FA contents will be prepared, and accelerated leaching tests will be conducted to measure key indicators such as compressive strength, porosity, leaching depth, and calcium ion leaching amount at different leaching ages. The influence of FA content on the leaching performance of shotcrete will be elucidated, and the characteristics of performance degradation along with microstructural deterioration mechanisms will be analyzed. The findings are expected to provide scientific basis that better reflects actual construction processes for the durability design, mix proportion optimization, and service life assessment of shotcrete in engineering applications such as tunnels.

2 Materials and methods

2.1 Materials

2.1.1 Cement

The cement used in this study was P·O 42.5 ordinary Portland cement produced by Youjiang Cement under Guangxi Denggao (Group) Tiandong Cement Co. The physical and mechanical properties of the cement are listed in Table 1, and the chemical composition is presented in Table 2. The test results confirm that the cement meets the relevant requirements of the Chinese standard *Silicate Cement and Ordinary Silicate Cement* (GB 175–2020).

2.1.2 Fine and coarse aggregates

Based on previous investigations, the fine aggregate used in this study exhibited a fineness modulus of 2.9, an apparent density of 2,701 kg/m^3, a bulk density of 1,634 kg/m^3, a stone powder content of 7.6%, and a methylene blue value of 1 g/kg. The coarse aggregate had a crushing value of 11%, a flakiness and elongation index of 4.2%, an apparent density of 2,720 kg/m^3, a water absorption of 0.2%, and a clay content of 0.6% (Liang et al., 2025). All aggregates conform to the requirements of the specification *Technical Specification for Highway Tunnel Construction* (JTG 3660–2020).

2.1.3 Fly ash

The fly ash used in this study was Class I fly ash, and its quality meets the requirements of the standard *Fly Ash Used for Cement and Concrete* (GB/T 1596–2017). The chemical composition of the fly ash is presented in Table 3.

2.1.4 Admixtures

2.1.4.1 Accelerator

As an indispensable admixture in shotcrete, the set accelerator can effectively accelerate the setting and hardening processes, enabling the shotcrete to rapidly attain the strength requirements specified by relevant standards. In this study, an alkali-free accelerator was used, with $Al_2(SO_4)_3$ as its main component. The initial and final setting times were 2 h 15 min and 9 h 50 min, respectively. The 1-day compressive strength reached 9 MPa, and the 28-day compressive strength retention ratio was 95% (Liang et al., 2025).

2.1.4.2 Water-reducing agent

A water-reducing agent is a concrete admixture that enhances the strength of shotcrete while reducing the mixing water demand. In this study, a high-performance water-reducing agent (FDN-C) produced by Shandong Wanshan Chemical was used. The admixture exhibited a water-reduction rate of 23.4%, a bleeding rate of 70.5%, and an air content of 2.1%. The differences in setting time between the initial and final setting were 207 min and 226 min, respectively. The compressive strength ratios at curing ages of 3, 7, and 28 days were 127%, 132%, and 134%, respectively (Liang et al., 2025).

2.1.5 Water

Two types of water were used in this study. Tap water was used for mixing the shotcrete specimens and met the technical requirements for concrete mixing water. Industrial distilled water was used to prepare the ammonium chloride solution for the leaching tests and met the standards for Grade I laboratory water.

TABLE 3 Chemical composition of fly ash.

Ingredients	Al_2O_3 (%)	SiO_2 (%)	SO_3 (%)	CaO (%)	Chloride Ion (%)
Content	24.2	45.1	2.1	5.6	0.015

TABLE 4 Mix ratio of shotcrete with different fly ash content (kg/m^3).

Number	w/b	Concrete	Fly ash	Manufactured sand	Stone	Water	Accelerator	Water reducer
S38	0.38*	474	0	918	782	180	31.5	2.7
S38F15	0.38*	412	62 (15%)	918	782	180	31.5	2.7
S38F20	0.38*	395	79 (20%)	918	782	180	31.5	2.7
S38F20	0.38*	379	95 (25%)	918	782	180	31.5	2.7

F denotes the percentage of fly ash replacement by mass of cement.

2.2 Experimental design scheme

2.2.1 Mix design for leaching specimens

Compared with ordinary concrete, determining the mix proportions of shotcrete is more complex, as any change in a single factor may significantly affect its overall performance. In this study, the fly ash content was used as the variable to investigate its influence on the performance and leaching resistance of shotcrete.

Fly Ash Replacement Ratio: Fly ash, as an industrial by-product, is widely used in concrete. It primarily contributes to concrete performance through four mechanisms: (1) Pozzolanic and cementitious behavior, which enhances later-age strength and improves the interfacial transition zone (Nivedha J. et al., 2025); (2) Filling and densification effects, where the fine fly ash particles reduce pore volume and refine the pore structure (Lin, 2020); (3) Water demand behavior and water-reducing effect: High-quality fly ash, owing to its ball bearing function, can improve the workability of concrete mixtures, reduce the water content per unit volume of concrete, decrease the drying shrinkage of hardened cement paste, and enhance crack resistance (Puthipad et al., 2016); (4) Lower early heat of hydration, which reduces early cracking and decreases the amount of $Ca(OH)_2$ in hydration products, thereby improving durability. Replacing part of the cement with fly ash reduces cement consumption and cost while improving durability (Kharade et al., 2022). Based on standards and previous studies, fly ash replacement ratios of 15%, 20%, and 25% were selected. The mix proportions of shotcrete with different fly ash contents are presented in Table 4.

2.2.2 Specimen preparation and curing

Shotcrete specimens were prepared using the wet-mix spraying method, following the requirements of the 'Technical Specification for Highway Tunnel Construction' (JTG/T 3660-2020). The production process is shown in Figure 1. After demolding, the specimens were placed in a standard curing room for 7 days. The cured slabs were then cut into 100 mm × 100 mm × 100 mm cube specimens. After cutting, the cube specimens were returned to the standard curing room and cured until 28 days.

2.2.3 Selection of leaching method

Concrete leaching under natural conditions progresses very slowly; therefore, accelerated leaching methods are commonly adopted in laboratory studies. At present, three major accelerated leaching methods are widely used: the deionized water method (Zou et al., 2022); the chemical reagent acceleration method (Phung et al., 2016); and the electrochemical acceleration method (Ryu et al., 2002). In this study, the chemical reagent acceleration method was selected. All specimens subjected to the leaching test were those cured under standard conditions for 28 days. To enhance the leaching rate, a 6 mol/L ammonium chloride (NH_4Cl) solution was used as the accelerated leaching agent. The corresponding chemical reaction equation is shown in Equation 1.

$$Ca(OH)_2 + 2NH_4Cl = CaCl_2 + 2NH_3 + 2H_2O \tag{1}$$

2.3 Testing methods

2.3.1 Compressive strength

According to the Chinese standard *Test Methods for Physical and Mechanical Properties of Concrete* (GB/T 50081—2019), unconfined compressive strength tests were conducted on shotcrete specimens. The specimens were cubic with dimensions of 100 mm × 100 mm × 100 mm. For each group, three parallel specimens were prepared and cured under standard conditions for 28 days. Subsequently, the specimens were subjected to erosion treatment, and the compressive strengths before and after erosion were measured to evaluate the strength variation induced by erosion. During testing, the loading rate was controlled at 0.3 MPa/s. Considering that the specimens were non-standard cubes, the measured compressive strength values were corrected using a conversion factor of 0.95. The compressive strength loss rate of shotcrete was calculated according to Equation 2.

$$\Delta f = \frac{f_0 - f_t}{f_0} \times 100\% \tag{2}$$

FIGURE 1
Process of making shotcrete slab on site.

Δf is the compressive strength loss rate at leaching time t; f_0 is the initial compressive strength at 28 days of standard curing (MPa); f_t is the compressive strength after leaching for time t (MPa); t is the leaching duration in days.

2.3.2 Porosity

In this study, the saturated–dry weighing method was employed to determine the porosity of shotcrete specimens during the erosion process, in order to analyze the temporal evolution of their pore structure. During the test, specimens cured to the specified age were first removed, and surface free water was wiped off. The specimens were then weighed using a high-precision electronic balance to obtain the saturated mass. Subsequently, each specimen was fully immersed and suspended in water for weighing, and the apparent mass in water was recorded. After the underwater weighing, the specimens were placed in a vacuum drying oven and dried at 105 °C until a constant mass was achieved. After cooling to room temperature, the dry mass was measured. Finally, based on the saturated mass, apparent mass in water, and dry mass, the porosity of the shotcrete specimens was calculated according to Equation 3.

$$\varphi_s = \frac{M_b - M_g}{M_b - M_f} \times 100\% \tag{3}$$

φ_s is the porosity of the specimen, M_b is the saturated mass (kg), M_f is the apparent mass in water (kg), M_g is the dry mass (kg).

2.3.3 Leaching depth

In this study, the phenolphthalein reagent method was employed to measure the leaching depth of the specimens. The specific procedure was as follows. First, each specimen was cut along the leaching direction. Then, the prepared phenolphthalein reagent was applied to the cross-section. The leached area appeared colorless, while the unleached area exhibited a purplish-red color. The leaching depth was defined as the distance from the specimen surface to the edge of the purplish-red area. Three measurement points were selected on each side of the purplish-red boundary. The leaching depth at each point was measured using a micrometer. Finally, the average leaching depth was calculated as the arithmetic mean of the 12 measured values.

2.3.4 Calcium ion leaching amount

The calcium ion concentration in the leaching solution was measured using a high-precision calcium ion meter manufactured by Shanghai Pante Instrument Co., equipped with a Ca-US calcium ion selective electrode imported from the United States. The measurement accuracy was ±1% F.S., and the measurement range was 5×10^{-7} to 1 M. Before each measurement, the solution in the leaching container was stirred thoroughly using a glass rod. A long pipette was used to extract 30 mL of solution from the upper, middle, and lower layers of the container. The samples were mixed evenly before measurement. Each measurement was repeated three times, and the average value was recorded. After testing, the sampled solution was returned to the container to maintain a constant solution volume throughout the entire leaching process.

2.3.5 SEM tests

The sample preparation procedure for SEM analysis was as follows. Cubic specimens were first cut from within 1 cm below the top surface of the leached test blocks. From these cubes, fragments containing both paste and aggregate, with each dimension less than 6 mm, were selected for SEM observation. The selected fragments were then placed into an ion sputter coater for gold coating prior to scanning. The remaining material was ground into powder, passed through a 400-mesh sieve, and stored in bags for subsequent use. A Hitachi SU-70 scanning electron microscope was employed for the observations. This instrument offers a resolution of 1.0 nm at 15 kV and 1.6 nm at 1 kV, and is capable of performing secondary electron imaging, backscattered electron imaging, and image processing for various solid samples.

3 Results and discussion

3.1 Compressive strength

The variation law of compressive strength with curing age for different fly ash dosages is shown in Figure 2. As can be observed from the figure, with the increase in fly ash dosage, the early-age strength of the specimens decreases progressively, indicating that the presence of fly ash reduces the initial compressive strength of the specimens. This is consistent with previous research findings (Ding et al., 2011). The reason is that the hydration reaction of fly ash proceeds more slowly than that of cement; the early strength of fly-ash shotcrete cannot be compensated in time, resulting in lower initial compressive strength as the fly ash dosage increases. At later ages, the compressive strengths of specimens S38F15 and S38F20 exceed that of S38, while S38F25 shows lower strength than S38, indicating that an appropriate amount of fly

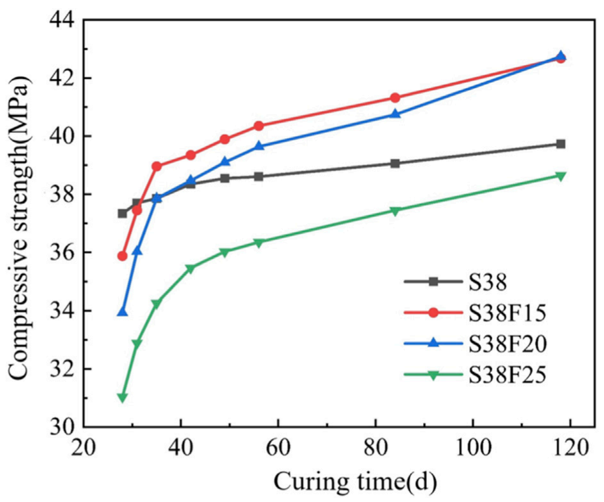

FIGURE 2
Relationship between compressive strength and curing time of specimens with different fly ash content.

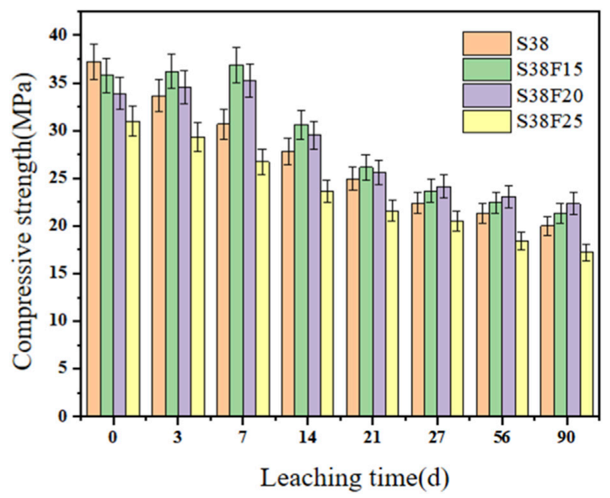

FIGURE 3
Relationship between compressive strength and leaching time of specimens with different fly ash content.

ash can improve the compressive strength of shotcrete, whereas excessive fly ash leads to a gradual decline in compressive strength.

The relationship between the compressive strength of specimens with different FA contents and the leaching time is shown in Figure 3. From Figure 3, it can be seen that the compressive strength of all specimens generally decreased to varying degrees as the leaching age increased. During the initial leaching period of 0–7 days, the compressive strength of specimens with FA contents of 15% and 20% gradually increased with continued leaching. This indicates that the rate of hydration exceeded the leaching rate in the early stage. Moreover, the lower porosity of FA-modified shotcrete helped inhibit the leaching reaction. The reason is that the hydration of FA proceeds slowly. After 28 days of curing, the active components in FA, such as SiO_2 and Al_2O_3, began to react with $Ca(OH)_2$ through the pozzolanic effect. This reaction produces calcium silicate hydrate with stronger cementitious properties, thereby enhancing the compressive strength of the shotcrete (Zhou et al., 2024). During the initial leaching period (0–7 days), a gradual decrease in compressive strength was observed for specimens with FA contents of 0% and 25% as leaching progressed. This indicates that excessive FA content can inhibit the development of compressive strength in FA-modified shotcrete. In the mid to late leaching stage (7–90 days), a substantial reduction in compressive strength was recorded for all specimen groups. This decline is attributed to the continuous dissolution of hydration products, such as $Ca(OH)_2$ and C-S-H, during leaching. Consequently, mass loss and increased porosity occur, which enhance permeation and diffusion effects, thereby accelerating the leaching process. Towards the end of the leaching period, the rate of compressive strength decline slowed down. However, specimens with 15% and 20% FA consistently exhibited higher compressive strength compared to those without FA. Therefore, based on compressive strength evaluation, an FA content of 15%–20% is considered beneficial for improving the leaching resistance of shotcrete.

The compressive strength loss rates of shotcrete specimens with different FA contents are shown in Figure 4. From the figure, it can be observed that the strength loss rates of specimens with 15%, 20%, and 25% FA are consistently lower than those of the non–fly-ash group. After 90 days of leaching, the strength loss rates of shotcrete specimens with 0%, 15%, 20%, and 25% FA are 46.25%, 40.5%, 34.13%, and 44.39%, respectively. Based on compressive strength loss, a FA content of 15%–25% helps improve the leaching resistance of shotcrete.

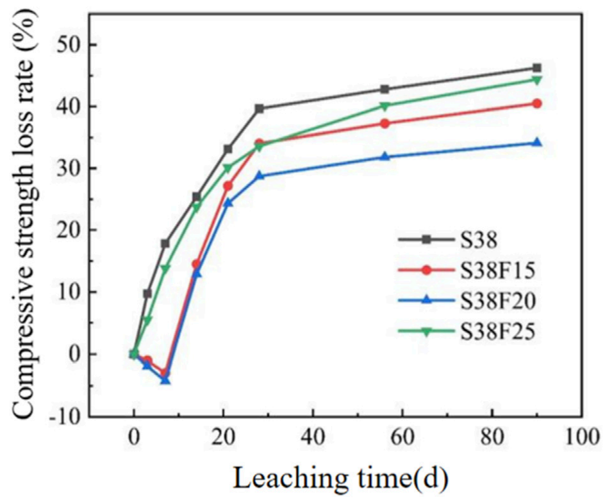

FIGURE 4
Compressive strength loss rate of specimens with different fly ash content.

3.2 Porosity

The variation in porosity with leaching time for specimens S38, S38F15, S38F20, and S38F25 with different FA contents during the accelerated leaching test using ammonium chloride is shown in Figure 5.

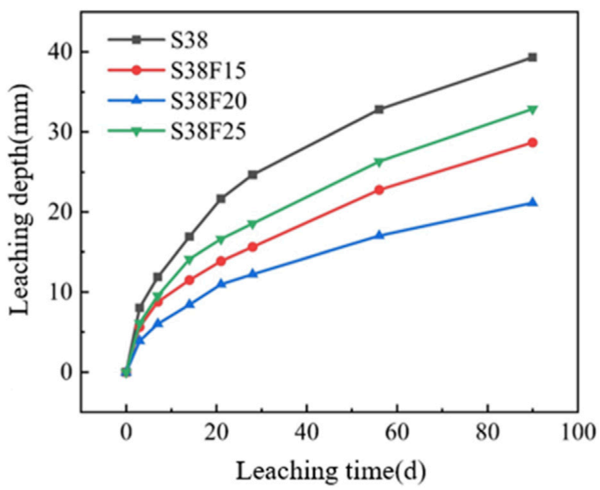

FIGURE 5
Relationship between leaching depth and leaching time of specimens with different fly ash content.

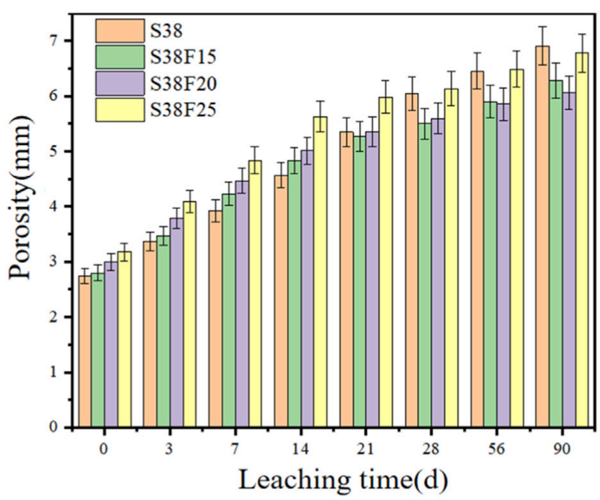

FIGURE 6
Relationship between porosity and leaching time of specimens with different fly ash content.

From Figure 6, it can be observed that before the leaching test, the porosities of shotcrete with 15%, 20%, and 25% FA are all higher than that of shotcrete without FA. Moreover, the higher the FA content, the greater the initial porosity of the shotcrete. This indicates that the incorporation of FA increases the initial porosity of shotcrete. As the FA content increases, the total amount of hydration products in early-age shotcrete decreases, and the secondary hydration rate of FA is slower than the cement hydration reaction. Therefore, early-age shotcrete still contains a large number of unhydrated FA particles, which cannot fully fill the pores of the specimens, resulting in higher initial porosity compared with ordinary shotcrete.

With the incorporation of FA, the increase in porosity after leaching becomes significantly smaller. After 90 days of leaching, the increases in porosity of specimens S38, S38F15, S38F20, and S38F25 are 4.14%, 3.48%, 3.09%, and 3.60%, respectively. This demonstrates that an appropriate amount of FA helps improve the leaching resistance of shotcrete. The reason is that with the continuous extension of the hydration time, the secondary hydration effect and micro-filler effect of FA gradually become evident. Newly generated C–S–H gels fill the capillary pores in shotcrete, densifying the structure and inhibiting the leaching process of shotcrete (Zhang et al., 2020).

Therefore, from the perspective of porosity, the optimal FA content for enhancing the leaching resistance of shotcrete is 20%.

3.3 Leaching depth

The variation in leaching depth of specimens with different FA contents over leaching time is shown in Figure 7. From the figure, it can be concluded that under the same leaching duration, the leaching depth of fly-ash shotcrete is always smaller than that of shotcrete without FA. The order of leaching-depth increase among mixtures is: S38F20 < S38F15 < S38F25 < S38. Due to the micro-filler effect and secondary hydration reaction of FA, which gradually take effect as hydration proceeds, the pore structure of shotcrete becomes optimized. In addition, part of the cement is replaced by FA, reducing the cement content and decreasing the amount of $Ca(OH)_2$ in hydration products. Since the first stage of leaching mainly involves the leaching of $Ca(OH)_2$, the incorporation of FA improves the leaching resistance of shotcrete. For specimen S38, which contains no FA, the micro-filler effect and secondary hydration effect do not occur. During leaching, newly formed hydration products cannot effectively fill the pores, and hydration products continuously dissolve out of the paste, leading to the fastest increase in leaching depth. After 90 days of leaching, the leaching depths of the four groups are 39.32 mm, 29.30 mm, 22.09 mm, and 33.00 mm, respectively. Among the four shotcrete mixtures, a FA content of 20% results in the smallest increase in leaching depth. Therefore, from the viewpoint of leaching depth, 20% FA provides the best leaching resistance.

The leaching depth of all specimens increases continuously with leaching time. In the later stage, the rate of increase slows. During the early stage (0–7 days), the increase in leaching depth is the fastest, with the order: S38 > S38F25 > S38F15 > S38F20. This is because, in the early stage, the secondary hydration of FA consumes $Ca(OH)_2$ and forms additional cementitious hydration products, which promote cement hydration and suppress the leaching process.

For S38F15, S38F20, and S38F25, the relationship between leaching depth and the square root of leaching time was fitted, as shown in Figure 8, and the fitted equations and correlation coefficients are listed in Table 5.

The fitted equation is shown in Equation 4:

$$D = k\sqrt{t} \tag{4}$$

In the above equation, D represents the leaching depth of the shotcrete (mm), k is defined as the diffusion coefficient (mm/$\sqrt{d}$), t denotes the leaching time(d).

As shown in Table 5, the leaching depth of shotcrete specimens with different FA contents exhibits a linear relationship with the square root of leaching time, which conforms to Fick's diffusion law. A similar conclusion was also reported by Segura et al. (2013).

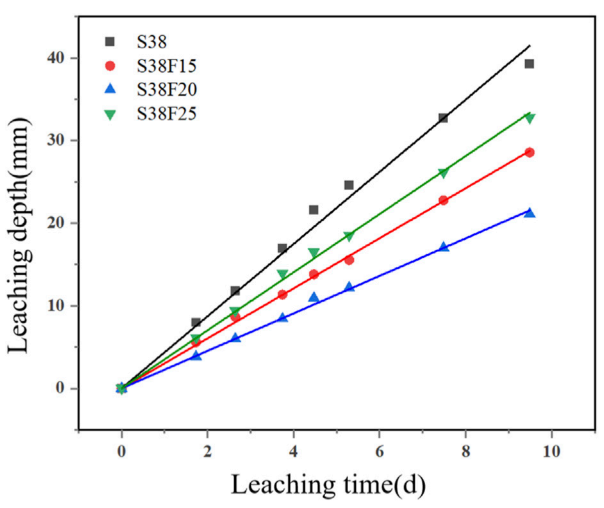

FIGURE 7
S38F15, S38F20 and S38F25 specimens leaching depth and leaching time square root fitting curve.

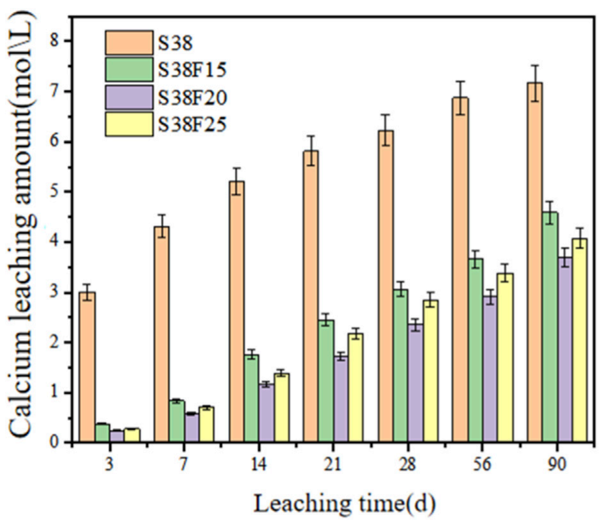

FIGURE 8
The relationship between calcium ion leaching and leaching time of specimens with different fly ash content.

TABLE 5 Fitting curve equation of leaching depth of S38F15, S38F20 and S38F25 specimens.

Specimen	Fitting curve equations	Correlation coefficient
S38	$D_0 = 4.3852\sqrt{t}$	0.99162
S38F15	$D_{15} = 3.0361\sqrt{t}$	0.99718
S38F20	$D_{20} = 2.2709\sqrt{t}$	0.99952
S38F25	$D_{25} = 3.525\sqrt{t}$	0.99938

The correlation coefficients exceeding 0.99 indicate a good fitting result. From Table 9, the diffusion coefficients for different mix proportions are: $k_0 = 4.3852$, $k_{15} = 3.0361$, $k_{20} = 2.2709$, $k_{25} = 3.525$. This demonstrates that the addition of FA can modify the diffusion coefficient (Kang et al., 2021). The coefficient k reflects the material's apparent diffusivity, which is related to factors such as the initial concentration of soluble substances in the concrete and the saturation concentration of the pore solution. The incorporation of an appropriate amount of FA promotes secondary hydration reactions, fills capillary pores, refines the pore size distribution, reduces porosity and pore connectivity, thereby decreasing the effective diffusion coefficient (Wu et al., 2024). As a result, the advancement rate of the leaching front slows down, corresponding to a reduced k value. In contrast, specimens without FA exhibit a relatively loose pore structure and more connected capillary pores, leading to lower diffusion resistance. This is reflected in higher k values and a faster leaching rate.

The order of diffusion coefficients is $k_{20}<k_{15}<k_{25}<k_0$, indicating that FA incorporation enhances the leaching resistance of shotcrete. From the perspective of leaching resistance, the optimal FA content is 20%, primarily due to the optimized pore structure resulting from the combined effects of physical filling and the pozzolanic reaction. At 20% FA content, the k value reaches its minimum, suggesting the most significant microstructural densification. However, when the FA content increases to 25%, the k value rises again (k25 > k20). This may be attributed to an excessive FA content diluting the cement concentration, which can lead to insufficient formation of the early hydration product skeleton (Luan et al., 2023). Additionally, some excess FA particles may not fully participate in the reaction, potentially introducing micro-defects or increasing water demand, thereby adversely affecting long-term densification.

3.4 Calcium ion leaching amount

The variation in calcium-ion leaching amount with leaching time for S38F15, S38F20, S38F25, and the control specimen S38 is shown in Figure 9.

From Figure 9, the calcium-ion leaching amount increases with the extension of leaching time for all mixtures. For shotcrete without fly ash (0% fly ash), the calcium-ion leaching amount increases rapidly during the early stage and gradually stabilizes. For shotcrete containing 15%, 20%, and 25% fly ash, the calcium-ion leaching amount increases linearly in the early stage. In the mid-leaching stage, the increase rate of fly-ash shotcrete becomes greater than that of the control specimen. In the late stage, the increase rate becomes even higher than in the early stage.

The total calcium-ion leaching amounts of the four mixtures are 7.2 mol/L, 4.6 mol/L, 3.7 mol/L, and 4.1 mol/L, respectively. From the perspective of calcium-ion leaching amount, 20% fly ash provides the best performance. Calcium hydroxide (CH) in cement hydration products is mainly produced by the hydration of C_3S and C_2S (Liu et al., 2018), accounting for 20%–25% of cement mass. Fly ash replaces part of the cement, reducing the CH content in the paste and thus reducing calcium-ion leaching. Moreover, the pozzolanic reaction of fly ash consumes $Ca(OH)_2$ and decreases the total amount of released calcium ions.

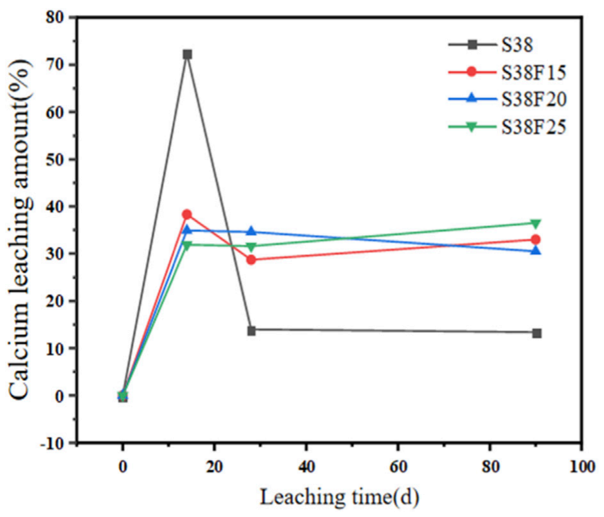

FIGURE 9
Calcium leaching rate.

Calcium leaching rate as shown in Figure 9. During the early stage (0–14 days), the calcium-ion leaching rate of the control specimen is much higher than that of fly-ash mixtures. As fly ash content increases, the early-stage leaching rate decreases. In the mid-stage (14–28 days), the leaching rates are 14.0%, 28.7%, 34.6%, and 31.6%, respectively. Although the rates differ, the actual dissolved amounts are similar: 1.01 mol/L, 1.32 mol/L, 1.42 mol/L, and 1.17 mol/L. In the late stage (28–90 days), fly-ash mixtures exhibit significantly higher leaching rates than the control. This is because the pozzolanic reaction of fly ash becomes more active and accelerates hydration, increasing the calcium-ion leaching rate.

By comparing compressive strength, porosity, leaching depth, and calcium-ion leaching, it is evident that fly ash improves the leaching resistance of shotcrete, with 20% being the optimal content. In practical engineering, an appropriate amount of fly ash can enhance durability while ensuring safety and economy.

3.5 SEM tests

Micrographs of specimens with different FA contents before and after leaching are presented in Figure 10. As shown in the figure, before leaching, the surface of the shotcrete specimens was relatively smooth, with a dense cement paste surface and good overall integrity. After 90 days of leaching, clear signs of deterioration were observed on the surface of the cementitious matrix. These included reduced flatness, increased roughness, dissolution of hydration products, and locally visible micropores formed due to the leaching of hydration products. From Figure 10b, it can be observed that the specimen without FA exhibited the most significant surface roughening after 90 days of leaching. The number and size of cracks in the cement paste increased, accompanied by numerous connected or isolated pores, indicating pronounced leaching damage. In contrast, the specimen with 20% FA maintained relatively better surface flatness under the same leaching conditions. Both crack development and pore formation were less pronounced, and the microstructural integrity was superior to that of specimens with other FA contents. These observations suggest that an appropriate amount of FA can effectively enhance the leaching resistance of shotcrete.

4 Conclusions and outlook

4.1 Conclusions

This study used fly ash content as the variable to systematically investigate the effects of fly ash on the leaching resistance and overall performance of shotcrete in ammonium chloride solution. The results show that the incorporation of fly ash has a certain improving effect on the leaching resistance of shotcrete, but the magnitude of improvement depends on a reasonable dosage.

1. Fly ash improves the mechanical properties of shotcrete to a limited extent. With the increase of fly ash content, the early compressive strength of shotcrete decreases, mainly due to the slower hydration reaction of fly ash and insufficient early hydration products. In the later stage of curing, the active SiO_2 and Al_2O_3 in fly ash react with $Ca(OH)_2$ to produce additional C–S–H and C–A–H gels, improving the compactness of the matrix and enhancing later-age strength. After 56 days of curing, the compressive strengths of specimens with 15% and 20% fly ash reach 40.35 MPa and 39.64 MPa, respectively, higher than the control mix by 4%–5%, indicating that an appropriate amount of fly ash can enhance the later-age mechanical performance and structural stability of shotcrete.
2. Fly ash effectively delays the progression of leaching in shotcrete. Under the same leaching age, the leaching depth of specimens with 20% fly ash is the smallest. The results show that the increase of fly ash content slightly increases initial porosity, but during leaching, the increase in porosity slows significantly. After 90 days of leaching, the strength loss rate of the specimen with 20% fly ash is the lowest at 34.13%, about 12% lower than the control group. This indicates that incorporating fly ash can effectively inhibit the advancement of the leaching front and slow the decalcification process.
3. Fly ash improves pore structure and enhances the material's durability. The porosity test results indicate that fly ash reduces pore connectivity and inhibits pore enlargement. Although the increase in leaching time causes an initial increase in porosity, the growth rate becomes significantly slower. During the early leaching stage, the porosity of specimens with 20% fly ash increases by 3.09%, significantly lower than the 25% fly ash mix. Due to the micro-filling and secondary hydration effects of fly ash, the matrix becomes denser, forming a more continuous skeleton structure and showing better resistance to ion penetration.
4. Leaching depth and calcium ion concentration both show that 20% fly ash yields the best performance. The calcium ion concentration increases continuously with leaching time, but the specimen with 20% fly ash consistently shows the lowest calcium ion leaching. After 90 days, the calcium ion concentration of the 20% fly ash specimen is 3.7 mmol/L, far lower than that of the control group (7.2 mmol/L). This

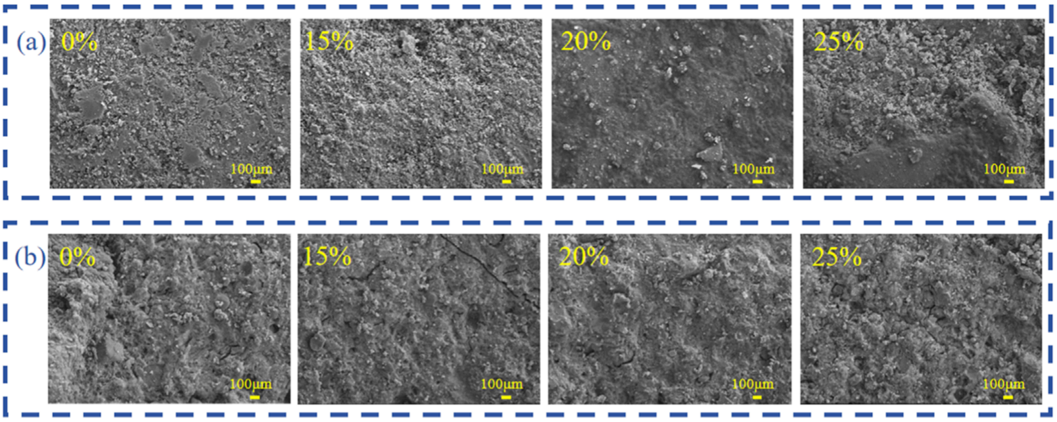

FIGURE 10
Micrographs of test specimens before and after leaching at different FA content levels. **(a)** Before leaching. **(b)** After 90 days of leaching.

indicates that fly ash effectively consumes $Ca(OH)_2$ through the pozzolanic reaction, reduces soluble calcium phases, and significantly enhances resistance to chemical leaching.

5. Comprehensive analysis shows that the pozzolanic reaction and micro-filling effect of fly ash are the key factors affecting the leaching resistance of shotcrete. Fly ash consumes $Ca(OH)_2$ through pozzolanic reactions, forms more stable C–S–H gel, and delays the outward migration of calcium ions. Its micro-filling effect refines the pore structure and improves density. Although excessive fly ash results in insufficient early hydration, moderate fly ash content effectively enhances the structure and durability during leaching.

In summary, fly ash can improve the physical, chemical, and durability properties of shotcrete. The optimal dosage is approximately 20%. This dosage not only meets mechanical performance requirements but also significantly enhances leaching resistance. These findings can provide scientific guidance and reference for mix design of shotcrete used in water-rich or chemically aggressive environments.

4.2 Outlook

This study systematically investigated the influence of FA content on the leaching resistance of wet-mix shotcrete and identified 20% as the optimal dosage. However, due to the limitations of the research scope, methods, and conditions, some constraints remain. To further deepen the understanding of the leaching resistance of FA-modified shotcrete and promote its engineering application, future research can focus on the following aspects:

1. This study employed only a 6 mol/L ammonium chloride solution for accelerated leaching tests. While this method effectively shortens the test duration, real-world leaching processes often involve complex factors such as wet-dry cycles, fluctuating ion concentrations, temperature variations, multi-ion interactions, and combined attacks from sulfates and carbonates. The static accelerated tests conducted in this study do not fully simulate long-term natural leaching conditions. Future research should investigate the performance degradation of shotcrete under the coupling effects of more realistic environmental factors, such as combined chemical attacks, freeze-thaw cycles, and mechanical stress, to establish more practical durability models.
2. The study focused solely on a blend of cement, FA, and admixtures. In practical engineering, material sources are diverse, and differences in microstructure caused by on-site spraying techniques can influence performance, potentially limiting the generalizability of the conclusions. Subsequent research should systematically examine the effects of different supplementary cementitious materials (such as slag and silica fume), types of accelerators, and their compatibility with cementitious systems. Comparative validation between laboratory-cast specimens and structures sprayed in the field should also be strengthened.
3. Building on the optimization of leaching resistance, research should explore the application technology of shotcrete with high-volume industrial by-products (e.g., FA, slag). This includes assessing their environmental benefits and economic viability over the entire life cycle, thereby promoting the green and low-carbon development of shotcrete technology.

Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author.

Author contributions

XZ: Writing – review and editing, Writing – original draft. QW: Writing – review and editing, Writing – original draft. XL: Writing – original draft, Conceptualization. LL: Writing – review and editing, Formal Analysis, Data curation. JL: Data curation, Writing – review

and editing, Formal Analysis. JW: Writing – review and editing, Methodology.

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Conflict of interest

Authors ZX and LX were employed by Guangxi Guilu Expressway Co, Ltd.

The remaining author(s) declared that this work was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Generative AI statement

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