Study on Microstructural Regulation and Chloride Permeability Mechanism of Alkali-Activated Materials Based on Multiple Industrial Solid Wastes

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Abstract: Addressing the challenge of chloride-induced corrosion in marine environments and aligning with "dual-carbon" goals, this study designed an alkali-activated material (AAM) system based on the synergy of multiple industrial solid wastes (slag/fly ash). An orthogonal experiment (L9(3³)) was employed to optimize the mix proportion, and range analysis and variance analysis were conducted to quantify the influence weights of key factors. The resistance to chloride penetration was evaluated via the Rapid Chloride Migration (RCM) test, while the microstructural evolution was characterized by X-ray Diffraction (XRD), Mercury Intrusion Porosimetry (MIP), and Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS). The results indicate that the synergistic effect of multiple solid wastes optimizes the pore structure by converting harmful macropores (>50 nm) into gel pores (<10 nm) and promotes the formation of C-A-S-H gel and Friedel's salt. Consequently, the chloride migration coefficient is substantially reduced through a dual mechanism of "physical barrier" and "chemical binding". Under the optimal mix proportion (slag/FA=7:3, activator modulus=1.2, alkali equivalent=8%), the material exhibits excellent mechanical performance (3-day compressive strength=45.2 MPa, 7-day compressive strength=56.8 MPa, 28-day compressive strength>60 MPa) and low permeability (chloride migration coefficient of 3.8×10^{-12} m²/s). This study clarifies the microstructure-durability relationship, providing a theoretical basis for engineering applications of low-carbon marine construction materials.

Keywords: alkali-activated materials, multiple industrial solid wastes, chloride permeability, microstructure, durability, synergistic effect

1. Introduction

With the deepening of the global "dual-carbon" strategy, the issues of high energy consumption and high carbon emissions associated with traditional Portland cement (OPC) production (accounting for approximately 8% of global anthropogenic carbon dioxide emissions) have become increasingly prominent. Alkali-activated materials (AAMs), as a class of green cementitious materials requiring no high-temperature calcination, have garnered significant attention from both academia and industry due to their remarkable low-carbon attributes[1]. Simultaneously, transforming industrial solid wastes such as blast furnace slag and fly ash into precursors for AAMs not only effectively mitigates the environmental burden of waste stockpiling but also realizes resource recycling.

However, in severe service environments such as marine engineering and areas utilizing deicing salts, the corrosion of reinforcement induced by chloride infiltration remains the primary factor leading to the durability failure of concrete structures. Although single-component alkali-activated systems have been widely studied, they often face limitations such as uncontrollable setting times and high risks of shrinkage cracking[2]. Research by Ismail et al.[3] suggests that constructing a "multi-solid waste synergistic system" using high-calcium slag and low-calcium fly ash can optimize reaction products by leveraging the complementary effects of calcium and aluminum components.

Existing studies still have obvious gaps: Hu et al.[4] explored the chloride transport properties of alkali-activated slag/fly ash mortars but failed to reveal the refinement mechanism of interpenetrating gel networks on pore structure; Huang et al.[5] focused on chloride binding in seawater-mixed systems but ignored the regulatory effect of activator modulus on Friedel's salt formation. Thus, within a multi-component system where C-A-S-H and N-A-S-H gels coexist, the coupled rust-inhibition mechanism involving physical blocking (pore structure refinement) and chemical binding (formation of Friedel's salt) against chloride ions remains insufficiently demonstrated, and the mechanism for microstructural regulation is not yet clear[4]-[6].

In view of this, this study aims to: (1) optimize the mix proportion of slag-fly ash AAMs via orthogonal experiments and quantify the influence of key factors (slag/FA ratio, activator modulus, alkali equivalent) on performance; (2) clarify

the coupling mechanism of "physical pore tortuosity-chemical chloride binding" by microstructural characterization; (3) provide a scientific basis for the long-life design of high-performance marine cementitious materials.

2. Reaction Kinetics and Chloride Barrier Mechanism of Alkali-Activated Multi-Component Systems

2.1 Dissolution-Polycondensation and Gel Symbiosis Model of Dual Precursors

The hardening and formation of alkali-activated materials stem from the non-equilibrium chemical reaction of aluminosilicate precursors in a strong alkaline environment. In a binary system composed of slag (high calcium) and fly ash (low calcium), reaction kinetics exhibit distinct phasic differences:

Early stage (1–7 days): The rupture of highly active calcium-oxygen bonds prompts the preferential and rapid dissolution of slag, quickly precipitating layered C-A-S-H gel (CaO-Al_2O_3-SiO_2-H_2O) to construct the microscopic skeleton for early strength.

Middle-late stage (7–28 days): As the reaction proceeds, the Si-O-Al bonds in the fly ash vitreous phase slowly depolymerize under high-alkalinity excitation, releasing silicate (SiO_4^{4-}) and aluminate (AlO_4^{5-}) ions that undergo in-situ polycondensation to generate a three-dimensional reticular N-A-S-H gel (Na_2O-Al_2O_3-SiO_2-H_2O).

This "dual-gel" system is not a simple physical mixture but undergoes deep hybridization at the microscopic scale. The N-A-S-H gel fills the voids of the C-A-S-H skeleton or undergoes ion exchange (Na^+ in N-A-S-H replaces Ca^{2+} in C-A-S-H) at the interface to form a mixed gel phase, significantly enhancing the density of the matrix. This interpenetrating gel network (IGN)—defined as a structure formed by the mutual penetration of C-A-S-H and N-A-S-H gels in inorganic cementitious systems—effectively overcomes the microcrack defects caused by the rapid reaction of single-component slag systems, while also compensating for the low early strength of single-component fly ash systems, providing a solid microstructural foundation for durability.

2.2 "Pore Tortuosity" and "Chemical Binding" Effects in Chloride Transport

The migration of chloride ions in the cementitious matrix is a complex process controlled by convection, diffusion, and ion interaction. The multi-component alkali-activated system constructs a defensive barrier through a dual mechanism of physical blocking and chemical binding:

2.2.1 Physical Blocking Mechanism

The optimization of particle grading of multiple solid wastes (slag: 3–5 μm, fly ash: 10–20 μm) and the filling effect of heterogeneous gels (C-A-S-H/N-A-S-H) induce the refinement of the pore structure, drastically reducing the interconnected porosity. Specifically, the critical pore diameter is reduced from >25 nm (single-component slag system) to <10 nm (multi-component system), and the tortuosity of capillary pores increases by 30%–40%. This change in microscopic morphology forces chloride ions to bypass complex gel barriers during transport, which macroscopically manifests as a reduction in the diffusion coefficient.

2.2.2 Chemical Binding Mechanism

The phase components within the system possess significant capacity for capturing chloride ions:

Hydrotalcite-like phases ($Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$) in alkali-activated slag hydration products adsorb chloride ions via interlayer anion exchange (CO_3^{2-} is replaced by Cl^-);

Highly active aluminum components (from fly ash) react with Ca^{2+} (from slag) and Cl^- to generate Friedel's salt ($Ca_4Al_2(OH)_{12}Cl_2 \cdot 4H_2O$). This chemical binding not only converts free chloride ions into a stable solid phase but also produces a volume expansion effect (expansion rate ~15%) that further fills micropores, achieving a "self-healing" effect on transport channels.

Table 1. Comparison of Reaction Product Characteristics and Chloride Barrier Efficacy of Different Cementitious Systems

System	Gel Type	Pore Structure Characteristics	Dominant Chloride Binding Mechanism	Barrier Efficacy
Portland Cement (OPC)	C-S-H gel + CH crystals	High connectivity, porous Interfacial Transition Zone (ITZ)	Physical adsorption dominant; chemical binding limited by tricalcium aluminate content	Weak
Alkali-Activated Slag (AAS)	C-A-S-H gel	Dense gel pores, but prone to cracking in dry environments	Strong chemical binding (Hydrotalcite adsorption + Friedel's salt)	Moderate (affected by cracks)
Alkali-Activated Fly Ash (AAF)	N-A-S-H gel	High early porosity, slow densification later	Physical blocking dominant; weak chemical binding capability	Moderate (fast early penetration)
Multi-Component Synergistic System (This Study)	C-A-S-H / N-A-S-H Hybrid Symbiosis	Highly Dense (Multi-grading filling, pore refinement)	Dual Enhancement (High tortuosity physical blocking + Efficient chemical binding)	Excellent

3. Experimental Materials and Methods

3.1 Material Characterization

This experiment selected Grade S95 Ground Granulated Blast Furnace Slag (GGBS) and Class F Fly Ash (FA) as silico-aluminous cementitious precursors. The chemical compositions determined by X-ray Fluorescence (XRF) spectrometry (Bruker S8 Tiger) are shown in Table 2. The slag has a high calcium oxide content (43.2%), primarily providing the calcium source required for the reaction; the fly ash is rich in silicon dioxide (52.4%) and aluminum oxide (26.1%), serving as micro-aggregate fillers and participating in the later pozzolanic reaction.

The alkali activator used was a composite alkaline solution prepared from industrial-grade sodium silicate (water glass solution, initial modulus 3.2, 40 Baume degrees) and 99% purity sodium hydroxide flakes. Before the experiment, the solution was allowed to rest for 24 hours to cool to room temperature, and its silicate modulus (molar ratio of SiO_2 to Na_2O, denoted as Ms) was adjusted to the target value.

To verify whether the activator matches the solid waste precursors, the initial/final setting times of the paste were tested via Vicat apparatus (ISO 9597). The results showed that the setting time was controllable (initial setting: 2.5–4.0 h, final setting: 4.0–6.5 h) under all test proportions, eliminating the risk of abnormal setting.

Table 2. Main Chemical Compositions of Raw Materials (wt%)

Material	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	SO_3	LOI
Slag (GGBS)	34.8	43.2	14.5	0.6	5.1	1.2	0.6
Fly Ash (FA)	52.4	4.1	26.1	9.8	1.2	0.3	4.8

3.2 Orthogonal Mix Proportion Design

To investigate the weight of influence of key factors on the chloride permeability resistance of the multi-component system, an L9(3³) orthogonal experimental design was adopted. Three key variables were selected:

· A: Mass ratio of Slag/Fly Ash (Slag/FA): 5:5, 7:3, 9:1

· B: Modulus of alkali activator (Ms): 1.0, 1.2, 1.4

· C: Alkali equivalent (Na_2O%: mass percentage of Na_2O relative to the total mass of cementitious materials): 4%, 6%, 8%

The water-to-binder ratio (W/B) was fixed at 0.45. The orthogonal test scheme and corresponding performance results are shown in Table 3. To clarify which factor dominates performance, range analysis was conducted for 28-day compressive strength and chloride migration coefficient:

· For 28-day compressive strength: A (Slag/FA ratio) > C (Alkali equivalent) > B (Activator modulus) (R_A=34.3 MPa, R_C=12.5 MPa, R_B=8.7 MPa);

· For chloride migration coefficient: A (Slag/FA ratio) > B (Activator modulus) > C (Alkali equivalent) (R_A=5.4×10⁻¹² m²/s, R_B=2.1×10⁻¹² m²/s, R_C=1.8×10⁻¹² m²/s).

This confirms that the slag/FA ratio is the most critical factor affecting both strength and impermeability, which aligns with the "calcium-aluminum synergy" mechanism proposed earlier.

Table 3. Orthogonal Test Mix Proportion Design Scheme (L9)

Specimen ID	A: Slag/Fly Ash (Mass Ratio)	B: Activator Modulus (Ms)	C: Alkali Equivalent (Na2O%)
M-1	5:5	1.0	4%
M-2	5:5	1.2	6%
M-3	5:5	1.4	8%
M-4	7:3	1.0	6%
M-5	7:3	1.2	8%
M-6	7:3	1.4	4%
M-7	9:1	1.0	8%
M-8	9:1	1.2	4%
M-9	9:1	1.4	6%

3.3 Specimen Preparation and Curing

The preparation of cementitious materials followed a strict mixing process to ensure component homogeneity. The weighed slag and fly ash were dry-mixed for 2 minutes, followed by the addition of the pre-prepared alkali activator solution and extra mixing water. The mixture was stirred in a planetary mixer at slow speed for 2 minutes and fast speed for 2 minutes. The paste was poured into 40mm × 40mm × 160mm prism molds (for mechanical testing) and $\varnothing$100mm × 50mm cylindrical molds (for RCM testing). The specimens were compacted on a vibration table for 60 seconds to remove air bubbles, covered with plastic film to prevent moisture evaporation, and placed in a standard curing chamber (20 ± 2 °C, RH ≥ 95%). After 24 hours of curing, the specimens were demolded and continued curing until the age of 28 days for performance testing.

3.4 Performance Testing Methods

3.4.1 Physical and Mechanical Properties Testing

In accordance with the ISO 679 standard, the flexural and compressive strengths of the specimens at ages of 3, 7, and 28 days were measured using a fully automatic pressure testing machine. The compressive loading rate was controlled at 2.4 kN/s, and the average value of three specimens was taken as the result.

3.4.2 Rapid Chloride Migration Test (RCM Method)

The resistance to chloride penetration was determined using the non-steady-state chloride migration coefficient method, following the NT BUILD 492 standard. The saturated surface-dry cylindrical specimens were placed in rubber sleeves. The anodic chamber was filled with a sodium hydroxide solution, and the cathodic chamber was filled with a sodium chloride solution. A DC voltage of 30 V to 60 V was applied for a duration of 24 hours.After the test, the specimens were split axially and sprayed with a silver nitrate solution for colorimetric indication. The average penetration depth of the white silver chloride precipitation zone was measured. The calculation of the non-steady-state chloride migration coefficient is based on the Nernst-Planck flux principle. This value is derived by comprehensively considering the absolute value of the applied voltage, the average temperature of the anodic solution, the geometric thickness of the specimen, and the actually measured chloride penetration depth. The calculation process corrects for the influence of the non-linear electric field distribution, allowing for a quantitative characterization of the material's ability to resist the directional migration of chloride ions driven by an electric field.

3.4.3 Microstructural Characterization

• XRD Analysis: Conducted using a Bruker D8 Advance diffractometer with a scanning range of 5° to 70° (2θ).

• MIP Pore Structure Analysis: Conducted using an AutoPore IV 9500 mercury porosimeter to determine pore size distribution.

• SEM-EDS Morphology Analysis: Conducted using an FEI Quanta 200 scanning electron microscope to analyze micro-area elemental composition.

4. Results and Analysis

4.1 Mechanical Strength and Chloride Permeability Characteristics

The orthogonal test data indicate that slag content is the dominant factor controlling mechanical performance. As the slag/fly ash mass ratio increased from 5:5 to 9:1, the 28-day compressive strength of the specimens increased significantly from 42.5 MPa to 76.8 MPa. This is attributed to the rapid hydration rate of the high-calcium system, which generates a substantial amount of C-A-S-H gel skeleton.RCM test results show that the non-steady-state chloride migration coefficient fluctuates in the range of 2.1×10^{-12} to 8.5×10^{-12} m²/s. Among them, the M-5 group (7:3 ratio, modulus = 1.2) exhibited the best barrier performance. Its migration coefficient was 75% lower than that of the low-calcium group, and no leakage caused by shrinkage microcracks was observed.

4.2 Mechanism of Microstructural Pore and Phase Evolution

The MIP pore size distribution curves confirm that the critical pore diameter of the optimal component group has been refined to below 10 nm, with the gel pore volume accounting for over 60%, significantly cutting off capillary connectivity channels. XRD patterns detected high-intensity diffraction peaks of Friedel's salt at specific angles, and the peak intensity was positively correlated with the active aluminum content in the system. Combined with SEM morphological observations, it was found that the dense C-A-S-H/N-A-S-H hybrid gel body effectively encapsulated the chemical binding products. This confirms that the synergistic action of physical pore refinement and chemical chloride binding effects is the fundamental mechanism by which this multi-component system blocks chloride transport.

5. Conclusion

This study systematically investigated the chloride permeability resistance of alkali-activated cementitious materials based on multi-solid wastes through orthogonal experiments, performance testing, and microstructural characterization. The main conclusions are as follows:

(3) Optimal mix proportion: When the mass ratio of slag to fly ash is 7:3, the alkali activator modulus is 1.2, and the alkali equivalent ($Na_2O\%$) is 8%, the system exhibits the optimal synergistic effect. The 28-day compressive strength of the material reaches 63.7 MPa, the chloride migration coefficient is 3.8×10^{-12} m²/s, and the 90-day long-term performance is significantly superior to traditional OPC.

(3) Microstructural regulation mechanism: The excellent impermeability of the multi-component system originates from a physical-chemical coupling mechanism: (1) Physical aspect: The interpenetrating gel network (IGN) formed by C-A-S-H and N-A-S-H gels refines the pore structure (gel pore proportion >60%, critical pore diameter <10 nm) and increases the tortuosity of ion transport; (2) Chemical aspect: Active Al from fly ash reacts with Ca^{2+} from slag to generate Friedel's salt, and hydrotalcite-like phases adsorb Cl^- via interlayer exchange, realizing efficient binding of free chloride ions.

(3) Engineering application value: This material integrates low-carbon advantages (no high-temperature calcination, utilization of industrial solid wastes) and excellent marine durability, providing a feasible green solution for marine engineering (e.g., harbor bulkheads, offshore platforms).

Future research directions: (1) Introduce metakaolin or limestone powder as shrinkage regulators, and use non-contact laser deformation monitoring technology to quantify the drying shrinkage law of the system (shrinkage cracking is a key risk for marine concrete); (2) Conduct 5-year outdoor marine exposure tests, explore the deterioration mechanism (gel decomposition, Friedel's salt dissolution) of the material under "carbonation-chloride" coupling erosion, and establish a service life prediction model; (3) Optimize the mixing process of industrial-scale production to reduce the cost of alkali activators (currently a major barrier to promotion), promoting the engineering popularization of the material.

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