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Review

A review of chloride transport in alkali-activated cement paste, mortar, and concrete

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HIGHLIGHTS

- A review and statistical meta-analysis of chloride transport in AACs is presented.
- The role of Ca^{2+} in glassy/non-glassy phases within precursors is elucidated.
- Higher Si:Al, Na:Al, and heat-curing, in general, improve chloride resistance.
- Limitations of current chloride transport measurement techniques are addressed.
- Research needs concerning chloride durability of AACs are identified and discussed.

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ABSTRACT

In this review, we present a meta-analysis of experimental data concerning chloride transport in alkali-activated cement (AAC) paste, mortar, and concrete. Sixty-six (66) studies were reviewed with a primary focus on measurement methodology, mixture design, and process-structure-property relationships related to microstructural development (i.e., porosity, pore size distribution), chloride diffusion, and chloride binding. In general, this review elucidates that aluminosilicate precursors with high amorphous contents and increased fineness that are activated with solutions of high alkalinity ($Na:Al \geq 0.75$) and silica content ($Si:Al \geq 1.5$) in combination with heat-curing (>40 °C) lead to microstructural characteristics (e.g., binder gel chemistries) that improve chloride durability, even though interactions between these factors are not well understood. Descriptive statistics of reported AAC paste porosities and AAC concrete chloride diffusion coefficients by aluminosilicate precursor (i.e., fly ash, slag, calcined clay, natural clay, binary blends) are presented, along with a summative discussion regarding new opportunities for advancing current scientific understanding of chloride transport in AACs.

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1. Introduction

Chloride-induced corrosion is a pervasive durability issue that continues to plague reinforced concrete structures worldwide. Approximately 3.4% of the global GDP ($2.5 Trillion USD) is spent each year to prevent, mitigate, and repair civil infrastructure damage due to chloride-induced corrosion [1]. Waterborne and airborne chlorides in marine environments and chlorides from surface-applied deicing salts exacerbate risks of chloride-induced depassivation and subsequent corrosion of mild steel in reinforced concrete structures. Fortuitously, the alkaline pore solution of ordinary portland cement (OPC) paste induces chemical passivation of mild steel at early ages by creating a thin, dense, self-protective layer of iron oxides and hydroxides [2]. However, transport of chloride ions through the cementitious matrix and its resulting accumulation at the steel surface can depassivate this protective layer. Chloride anions react with metal cations, creating corrosion products and liberating protons that result in a more local acidic environment, promoting further depassivation.

Alkali-activated cements (AACs) have emerged as a potential alternative to OPC in recent years because of comparable—and occasionally superior—mechanical and durability properties and potentially lower environmental impacts [3–5]. AACs are synthesized by dissolving an aluminosilicate material (e.g., fly ash, slag, metakaolin) in a highly alkaline solution, most often in the presence of soluble silicates [6]. Precursor dissolution enables gelation and subsequent formation of an inorganic aluminosilicate polymer comprised of silica and alumina tetrahedra linked in three dimensions [4,7]. For a comprehensive review of AACs and more detailed information regarding their synthesis, microstructure, and material properties, see [3,4]. Other helpful reviews concerning the durability of AAC materials include [5,8,9], and [10].

The objective of this work—and what distinguishes it from prior literature reviews—is to provide a comprehensive overview of the process-structure-property relationships of AACs as they pertain to chloride transport. Sixty-six (66) studies were reviewed with a primary focus on measurement methodology, mixture design, and process-structure-property relationships related to microstructural development (i.e., porosity, pore size distribution), chloride diffusion, and chloride binding. These studies were selected because they explicitly investigated how physical and chemical properties of aluminosilicate precursors, activator content, and/or other processing parameters impact microstructural development and properties that affect chloride transport in AAC paste, mortar, and/or concrete. The content of this review is organized into the following main topics: (1) chloride transport mechanisms and characterization methods, (2) factors that influence microstructural development and material properties that affect chloride transport in AACs, (3) a meta-analysis of published experimental data, and (4) limitations of characterization methods for chloride intrusion in AAC paste, mortar, and concrete. We conclude this review by highlighting challenges, limitations, and future opportunities to advance scientific understanding of chloride transport in AACs.

2. Mechanisms and measurement of chloride transport in AACs

Chloride transport through porous cementitious materials is governed by three primary mechanisms: hydrostatic pressure, capillary absorption, and diffusion. Hydrostatic pressure drives chloride ions into the cement matrix by pressure gradients. If a hydraulic head of seawater is applied to a concrete surface, for example, chlorides will penetrate the surface [11]. In contrast, capillary absorption is driven by small intermolecular forces within the pores sized in the 10 nm–10 μm range, enabling absorption of ionic liquids without assistance from external forces. Chloride ions also diffuse through cementitious media *via* concentration gradients. Provided that the concrete is sufficiently saturated (>80%) [12], high concentrations of chloride ions will diffuse into the bulk through all interconnected pores where there is an initially lower concentration of chloride ions.

Hardened-state material properties, including porosity, pore solution chemistry, pore size distribution, tortuosity, and chloride binding potential, are well known to affect the rate of chloride transport in cementitious materials [11], and although their measurement has been standardized for OPC concrete, oftentimes all of them are not assessed in one study. Standard characterization methods for ion transport in AAC concrete, however, are much less established. While AAC-specific tests and protocols for chloride ion transport are still emerging (see Section 4), early attempts at understanding mechanisms that underlie/influence these effects have been adapted from tests developed for OPC concrete. Specifically, these tests (see Table 1) include direct and indirect physical tests (i.e., sorptivity, porosimetry, permeability, water absorption), chemical tests (i.e., chloride penetration), and electrical tests (i.e., resistivity). Indirect physical tests focus on microstructural characterization (i.e., pore size, total porosity) or utilize proxy measurements (i.e., water absorption, permeability) and relate these properties to durability. While indicative of microstructural characteristics, these physical tests cannot directly measure chloride diffusion or chloride resistance, but they are a useful way to estimate how AACs may perform in the presence of an ionic chloride solution. Chemical tests (e.g., chloride ponding) are often used to directly assess (1) time-dependent chloride penetration, (2) chloride content through the sample thickness using an indicator such as $AgNO_3$, and (3) chloride binding using solubility techniques [13,14]. From these tests, a diffusion rate (i.e., diffusion coefficient) can be calculated. Lastly, resistivity methods are utilized to provide a quantitative measure chloride ion transport, where decreased resistivity indicates higher degrees of chloride penetration. As is further discussed in the context of our statistical analysis of reviewed literature in Section 4, each of these methodologies has inherent limitations in their measurement that must be under-