



# Comparing ion diffusion in alternative cementitious materials in real time by using non-destructive X-ray imaging



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## ABSTRACT

Alternative cementitious materials (ACMs) are receiving increasing attention worldwide but there is a lack of knowledge around the resistance of these materials against harmful ion intrusion. In addition, current accelerated test methods that measure ionic diffusion under an electric field are not reliable when comparing binders with vastly different pore solution chemistry. This paper overcomes these issues by using laboratory transmission X-ray microscopy (TXM) and micro X-ray fluorescence ( $\mu$ XRF) imaging to make real-time measurements of ion diffusion in paste and mortar samples for five commercially available ACMs and an ordinary portland cement.

The results compare the apparent ion diffusion rate, quantify the change in the ion diffusion rate over time, and give insights into ion binding. The results show that after 42 d of ion exposure that the samples made with calcium aluminate cement had the lowest rate of ion penetration while the samples with alkali activated and calcium sulfoaluminate cement had the greatest rate of ion penetration. The portland cement had an ion penetration level that was between these two. Also, both the alkali-activated and calcium sulfoaluminate samples showed a decrease in the rate of penetration over time. These measurements are important to quantify the sustainability of ACMs, better justify their uses where durability are a concern, and guide future durability testing for these promising materials.

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## 1. Introduction

Manufacturing portland cement accounts for approximately 5% of anthropogenic CO<sub>2</sub> emission [1]. The use of novel alternative cementitious materials (ACMs) with lower embodied energy than portland cement is one way of reducing CO<sub>2</sub> emission associated with concrete production [2–5].

Calcium aluminate cements (CAC), calcium sulfoaluminate cements (CSA), and alkali-activated binders (AA) show potential as alternatives to portland cement [3,5]. CACs contain around 40–50% of Al<sub>2</sub>O<sub>3</sub> as a principle oxide, mainly in the form of monocalcium aluminate (CA), which reacts with water to give calcium aluminate hydrates (C-A-H) [3,6]. CSA cements are composed of ye'elimite (C<sub>4</sub>A<sub>3</sub>S) around 30–70% as main mineral phase, belite (C<sub>2</sub>S), and anhydrite or gypsum [7,8]. The primary products of CSA cements are ettringite, monosulfate, and strätlingite [3]. Alkali-activated binders can be produced by mixing an alkaline solution with a

reactive solid aluminosilicate powder such as fly ash, blast furnace slag, or metakaolin [3,9,10]. The reaction product of AA binders is variant as a consequence of the chemical differences between various precursors and the influences of different activator concentrations and chemistries [11,12].

ACMs are currently receiving increasing attention worldwide while there is a lack of knowledge around the durability of these materials in harsh environments [3,5,13]. A number of durability problems are caused by external fluids penetrating into cement-based materials [14–17]. Fluids which contain potentially harmful ionic species can lead to damage from corrosion, sulfate attack, alkali silica reaction, bulk freeze thaw, and salt scaling [18,19]. Therefore, the ion transport properties of cement-based materials play an important role in the durability performance of concrete structures [20,21]. There are a limited number of studies concerning the penetration of ions in ACMs [13,22–26]. In addition, current accelerated test methods based on ionic diffusion under an electric field are not a reliable indicator of ion diffusion when comparing ACMs because of the difference in the pore solution chemistry [13,27].

This work uses transmission X-ray microscopy (TXM) to image

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the movement of ions in ACMs. This technique is rapid, non-destructive, and able to provide useful and direct observations of ion movement in cement-based materials at a useful length scale. This method is based on measuring X-ray attenuation differences of paste or concrete. In TXM different materials will appear to have different gray values depending on their X-ray absorption. While this technique does not provide direct compositional information about the investigated materials, it does provide clues about compositional consistency [28,29].

In this study, the moisture penetration is imaged with the aid of adding potassium iodide (KI) as a contrast agent or tracer. Iodine is strongly X-ray attenuating because of its high atomic number. Furthermore, iodide and chloride ions are similar in size (iodide radius is 206 p.m. versus a chloride radius of 167 p.m.). This property makes iodide an excellent tracer for fluid transport study of concrete with X-rays [30,31]. As the tracer penetrates into the material it is possible to see the corresponding changes in X-ray absorption or gray value in the radiograph. By taking images over time then a rate of penetration or an effective transport constant can be calculated. Since this technique is non-destructive, the same sample can be monitored over time and under different conditions. The method requires minimal sample preparation and the technique can image at a spatial resolution of 200 nm to 20  $\mu\text{m}$  with laboratory equipment.

This work aims to use TXM to investigate time-dependent iodide diffusion for paste and mortar samples with three general classes of ACMs (CAC, CSA and AA binders) as well as portland cement. These same samples were investigated with micro X-ray fluorescence ( $\mu\text{XRF}$ ) in order to compare their results.  $\mu\text{XRF}$  is similar to bulk X-ray fluorescence (XRF) but this method uses a polycapillary optic to focus X-rays to a size of approximately 50  $\mu\text{m}$  in diameter, whereas bulk XRF investigates the sample with a 1 cm diameter investigation area. In addition,  $\mu\text{XRF}$  provides individual compositional maps which can be combined into a single map that simultaneously provides unique compositions and location [32,33]. Furthermore,  $\mu\text{XRF}$  imaging was used to compare iodide and chloride concentration profiles and diffusion coefficients in paste mixtures with different types of binders.

## 2. Experimental methods

### 2.1. Materials

Six commercially available binders were used in this study: an ordinary portland cement Type I/II according to ASTM C 150 (OPC); a calcium sulfoaluminate cement (CSA2); a calcium sulfoaluminate cement with a polymer additive to reduce the porosity (CSA2B); a calcium aluminate cement (CAC3); a blended cement consisting of primarily calcium aluminate and OPC with a small amount of gypsum (CAC2); and an alkali activated binder with a Class C fly ash according to ASTM C 618 as a solid precursor (AA1). These binders are commercial products and so in depth investigation of their formulation was not within the scope of the research. However, the chemical composition of binders, measured using bulk XRF, is provided in Table 1. More details can be found in other publications [5].

A commercial two component activator was used to prepare the AA1 paste and mortar mixtures. Polycarboxylate based high-range water-reducing (HRWR) admixture was used to improve the workability of the fresh paste and mortar mixtures for all binders except mixtures with CAC3 and AA1. The dosage level was chosen for each mixture to match the dosage needed to provide a consistent slump in concrete mixtures. These details are provided in Table 2. A food-grade citric acid was used as a retarder to control set time of CSA2, CSA2B, and CAC2 cements. In addition, plasticizer –

**Table 1**  
Chemical composition of binders with bulk XRF (% weight).

Binder type	OPC	CSA2, CSA2B	CAC2	CAC3	Fly Ash
SiO <sub>2</sub>	17.39	14.24	14.95	5.50	38.24
Al <sub>2</sub> O <sub>3</sub>	4.87	14.84	12.03	45.16	17.87
Fe <sub>2</sub> O <sub>3</sub>	4.71	1.12	2.66	6.90	5.88
CaO	65.15	49.23	55.15	37.68	24.75
MgO	1.40	1.55	2.57	0.22	6.24
SO <sub>3</sub>	2.51	13.55	7.72	0.07	1.56
K <sub>2</sub> O	0.48	0.67	0.83	0.26	0.34
Na <sub>2</sub> O	0.46	0.21	0.28	0	1.85
P <sub>2</sub> O <sub>5</sub>	0.13	0.11	0.14	0.09	–
TiO <sub>2</sub>	0.39	0.70	0.51	2.11	–
Mn <sub>2</sub> O <sub>3</sub>	0.11	0.02	0.16	0.02	–
SrO	0.15	0.20	0.21	0.04	–
ZnO	0.03	0.01	0.11	0	–
Cr <sub>2</sub> O <sub>3</sub>	0.09	0.05	0.07	0.089	–
LOI	2.12	3.51	2.61	1.86	0.20

set retarder (PSR) was used in preparation of CAC3 samples to assure a good workability and a delay of set. The dosages of these set modifying admixtures were chosen based on isothermal calorimetry experiments so that rapid hydration began at 2 h. More details can be found in other publications [5]. The fine aggregate is a natural river sand with a specific gravity of 2.60, and an absorption of 0.86% was used to prepare the mortar mixtures.

### 2.2. Mixture proportion and sample preparation

A cement paste mixture and a mortar mixture with water-to-binder ratio (w/b) of 0.40 were investigated for all binders except AA1. Based on manufacturer recommendation, a w/b of 0.21 was used to make AA1 paste and mortar mixtures. For AA1 the water is used as a plasticizer as per the manufacturer recommendations. This water content was chosen as it provided an equivalent slump in concrete mixtures made with these materials [34]. The paste and mortar mixtures were prepared according to ASTM C 305 and the mixture proportions are given in Table 2. In the mixing of AA1, the Class C fly ash was used in replacement of the cement and the activator was added to the water. The activator was used at a dose of 4% by weight of the fly ash as per the manufacturer recommendations. The mortar mixture contains 52% aggregate by weight for all binders except AA1 mortar mix which consists 58% aggregate by weight. This higher volume of sand for AA1 was used because of the different specific gravity of the fly ash compared to the other binders investigated.

Cylindrical micro vials with inside dimension of 9.5 × 46 mm were used to cast the samples. A lid was used to seal each vial. Six samples were made from each mixture. Three samples for each ponding solution and for both the KI and NaCl solution. The vials were only partially filled so that there was room to provide solution above them. These samples were cured for 14 d in a sealed condition at 23 °C.

### 2.3. Degree of saturation and porosity

This study measured the porosity and degree of saturation (DoS) of six paste samples with dimension of 9.5 × 35 mm that were cured in two different conditions as per ASTM C 642. Three samples were cured for 7 d and the other three for 35 d in a sealed condition at 23 °C. The samples were vacuum-saturated with water for 24 h to measure the saturated surface-dry mass in air. Next, the weight of the saturated samples immersed in water was measured and then the samples were dried in an oven at 50 °C and weighed again. In all measurements, it was assumed that the sample had reached mass equilibrium when the mass change was less than 0.03% during a 24 h period.

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