



The impact of carbonation on the microstructure and solubility of major constituents in microconcrete materials with varying alkalinities due to fly ash replacement of ordinary Portland cement



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ABSTRACT

The impact of alkalinity on the carbonation reaction in microconcrete mortars was assessed by evaluating the changes in the microstructure, solubility, and migration of major constituents (i.e., calcium, aluminum, and silicon) for cases of partial replacement of the Portland cement with different fly ashes having varying alkalinity. Several experimental techniques (i.e., SEM-EDS, U.S. EPA Method 1313, TIC, and TGA) were used and compared as tools to characterize changes due to the carbonation reaction. The rate and extent of carbonation was inversely related to the alkalinity of the material as evident by the increase in carbonation depth, reduction of the natural pH of the material, extent of the changes in the microstructure, and extent of reaction. Calcium migrated to the carbonated region while conversely silicon migrated from the carbonated region in response to relative solubility and therefore different diffusivity in the carbonated and uncarbonated regions for each constituent.

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1. Introduction

The service life of cement-based materials is a critical parameter for management of virgin and secondary materials in the cement and concrete applications. Structural degradation is especially important for cementitious materials in nuclear waste applications due to the potential for release of radioactive constituents which could adversely affect human health and the environment. Cementitious materials for nuclear waste management include binding matrices for low-activity waste forms and physical barriers such as grouts for waste tank capping, concrete vaults for waste containment, and mass pours for reactor entombments [1]. Often these materials contain supplemental cementitious materials (SCMs) designed to modify material performance. In these applications, it is desirable that cementitious materials maintain structural, hydraulic and chemical performance to the extent possible for lifetimes up to thousands of years. Although many of the mix designs for nuclear waste applications rely on coarse aggregate, the study of chemical performance and degradation often focus on the reactions and structure of the cement paste or of cement mortars. With regard to leaching and degradation of commercial concretes, microconcretes (i.e., mortars with high levels of fine aggregate that mimic concrete rheology) have been shown effective as surrogates for concretes containing coarse aggregate [2,3].

Much of the physical and chemical durability of cementitious materials has been attributed to the formation of a highly-buffered alkaline matrix consisting mainly of calcium-silicate-hydrates (C-S-H) and portlandite [Ca(OH)₂]. However, a key mechanism for degradation of cementitious matrices is reaction of the alkaline matrix with atmospheric or soil-gas carbon dioxide (CO₂), also known as carbonation. Over the extended material performance intervals for nuclear waste applications, degradation due to carbonation can potentially lead to the release of radionuclides [4]. Atmospheric or soil-gas CO₂ reacts with dissolved minerals in the cement pore water resulting in (i) depletion of matrix alkalinity which neutralizes pore water and affects the solubility of pH-dependent constituents and (ii) precipitation of relative insoluble carbonate phases which alters the pore structure of the matrix. In extreme cases, carbonation may lead to depassivation of reinforcing steel, physical degradation of the cementitious material, and loss of strength due to cracking in both nuclear and non-nuclear applications. Therefore, considerable effort has been placed on characterizing the primary degradation mechanisms of cementitious materials including the penetration of CO₂ and reaction rate of carbonation [5–8].

Microstructural analysis is key to understanding the overall behavior of the material, especially under conditions where changes in the microstructure and porosity occur due to the formation of carbonated products [9]. Analysis of the microstructure can identify the composition, morphology and spatial distribution of phases present in the system providing useful information on the mechanisms of hydration or degradation [10]. Characterization of the cement microstructure and redistribution of elements as a result of carbonation may lead to a better

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understanding of the macroscopic deterioration that occurs in concrete over extended periods.

This study evaluates the impact of material alkalinity on the carbonation process for three microconcrete materials with different alkalinities by assessing the changes in solubility of the major constituents (i.e., calcium, aluminum, and silicon), microstructure, distribution of elemental constituents across a reacted carbonated front, extent of reaction, and reaction capacity. The results of this study are intended as input to a framework to predict material durability in commercial and nuclear applications and the migration/release of heavy metals and radionuclides from cementitious materials used in nuclear waste applications.

2. Carbonation in cementitious media

The penetration CO₂ gas from air or soil media into a porous cement material results in subsequent reaction of aqueous CO₂ with hydration minerals including portlandite, C-S-H, and ettringite [Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O] to form carbonated products [11,12]. In particular, the reaction of CO₂ with portlandite is of interest because of the abundance of portlandite in the material and because the reaction decreases the pH of the material. Papadakis et al. [7] represented the overall reaction between portlandite and CO₂ as two steps: the dissolution of the portlandite (Eq.1) and the overall carbonation reaction (Eq.2), which is comprised of other elementary steps.



These steps are cyclic in that the consumption of free hydroxide ions in the pore solution (Eq. 2) results in further dissolution of portlandite leading to depletion and reduced pH in carbonated materials. Localized depletion of portlandite results in subsequent decalcification of C-S-H [7,13] according to Eq. 3:



Since portlandite is more soluble ($K_{\text{sp}} = 5.5 \times 10^{-6}$ at 25 °C) than CaCO₃ ($K_{\text{sp}} = 4.7 \times 10^{-9}$ at 25 °C) [14] and there is a shift in the pH of the material, the concentration of constituent ions in the pore solution is expected to be different in the carbonated region of the material compared to the uncarbonated region. Studies of the changes in the leaching behavior upon carbonation of cementitious materials indicate that the differences in the pore solution concentrations of the major constituent ions (i.e., calcium, aluminum, and silicon) will significantly impact the time-dependent leaching of these constituents from concrete materials [2,15–17]. Therefore, leaching tests intended to characterize the liquid-solid partitioning of calcium, aluminum, and silicon in solid materials can be used to identify changes in constituent solubility and concentration of constituents in the pore water solution due to the phase changes associated with the carbonation reactions.

The carbonation of cementitious materials is a complex process that is further complicated by the addition of SCMs which may be used as replacement for a portion of the Portland cement component in blended cementitious materials. Replacement of a fraction of the Portland cement with SCMs often improves the mechanical performance of these systems and reduces the need for virgin cement. For example, the addition of coal combustion fly ash promotes the conversion of portlandite to C-S-H during hydration and, hence, refines the microstructure of the concrete which ultimately affects the transport properties of the matrix which controls the diffusivity of CO₂ [18,19]. Previous studies suggest that the presence of fly ash increases the rate of carbonation because of a change in material alkalinity and the availability of portlandite [18,20–22]. Models have been designed to predict the penetration depth of the carbonation reaction front in concrete materials

with fly ash replacement [23,24], yet more effort is needed to characterize the evolution of the microstructure coupled with the elemental distribution for these materials. However, since the amount of alkalinity provided by fly ash can vary significantly based on coal source and combustion configurations [25], the uncertainty about prediction of the carbonation rate and extent of microstructural effects increased.

3. Materials and methods

3.1. Microconcretes

Microconcrete mortars with different levels of total alkalinity were prepared by mixing Type I/II ordinary Portland cement (OPC), fly ash (FA02 or FA39), river sand (fine aggregate), and water according to the mix designs shown in Table 1 [26]. FA02 is a low calcium (1.9% by mass) Class F fly ash from the combustion of bituminous coal and FA39 is a high calcium (17.1% by mass) Class C fly ash from the combustion of sub-bituminous coal. The microconcretes include a control material with no fly ash (M-00), a blended microconcrete with 45% of the OPC fraction replaced by FA02 (M-02), and a blended microconcrete with 45% replacement of OPC with FA39 (M-39). A sieve analysis was performed on the fine aggregate (Table S1). The material source details and characteristic leaching data for these materials have been reported elsewhere [3]; however, the naming scheme for the microconcretes has been simplified to improve the presentation clarity of this study.

For each microconcrete, ten cylindrical monoliths (6.5 cm diameter × 9.0 cm height) were cast and cured for 6 months at 100% relative humidity (RH) in a sealed 19-liter bucket maintained at ambient temperature (21 ± 2 °C). After the 6-month cure, three of the monoliths for each microconcrete were carbonated for an additional 6 months in a Thermo Scientific 3531 environmental chamber (Thermo Fisher Scientific, Inc., Waltham, MA) maintained at 5% CO₂, 65% RH, and ambient temperature. These carbonated materials are denoted as samples MC-00, MC-02, and MC-39. In parallel, three monoliths for each microconcrete, labeled M-00, M-02 and M-39, remained in the sealed buckets for an additional 6 months of curing without exposure to CO₂. Four monoliths for each microconcrete were collected after the initial 6-month cure and crushed using a parallel plate grinder until at least 85% by mass (wt%) of the material was <2 mm in diameter. Half of this granular material was placed in the same carbonation chamber with the monolith samples for 6 months and the remaining half was returned to the sealed bucket for additional 6 months of curing. For the purposes of these experiments, particle size reduction was intended to maximize the extent of carbonation over 6 months by increasing the surface area exposed to CO₂. In addition, United States Environmental Protection Agency (U.S. EPA) Method 1313, thermogravimetric analysis (TGA), and total inorganic carbon (TIC) used to characterize the carbonation reaction require a size reduced material and therefore the crushed microconcretes were used in these test methods. A summary of the microconcretes curing, crushing, carbonation conditions, and test method for each material is summarized in Table 2.

Table 1
Microconcrete formulations.

	Control	Blend	Control	Blend
Nominal Mix (kg/m ³)	514	514		
Fly ash replacement (%)	–	45		
	Composition (wt%)		Composition (kg/m ³)	
Portland cement	22.2	12.2	301	165
Fly ash	–	10	–	136
Water	9.9	10.1	135	136
Fine aggregate	67.9	67.7	940	920

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