An alternative mechanism for accelerated carbon sequestration in concrete

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ABSTRACT

The increased rate of carbon dioxide sequestration (carbonation) is desired in many primary and secondary life applications of concrete in order to make the life cycle of concrete structures more carbon neutral. Most carbonation rate studies have focused on concrete exposed to air under various conditions. An alternative mechanism for accelerated carbon sequestration in concrete was investigated in this research based on the pH change of waters in contact with pervious concrete which have been submerged in carbonate laden waters. This may be pertinent for applications of concrete reuse in marine or other aqueous applications such as jetties and riprap. The results indicate that the concrete exposed to high levels of carbonate species in water may carbonate faster than when exposed to ambient air, and that the rate is higher with higher concentrations. Validation of increased carbon dioxide sequestration was also performed via thermogravimetric analysis (TGA). It is theorized that the proposed alternative mechanism reduces a limiting rate effect of carbon dioxide dissolution in water in the micro pores of the concrete.
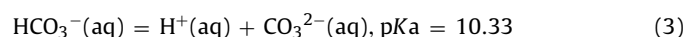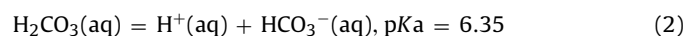
1. Introduction

The concentration of carbon dioxide is thought to have increased considerably since the industrial revolution due to anthropogenic activity and may have an impact on global climate variability. The production of Portland cement contributes to carbon dioxide emissions through both energy usage and calcination, the chemical reaction whereby calcium carbonate dissociates into carbon dioxide and calcium oxide, a major component of portland cement. This cement is then used to make Portland cement concrete, widely used for structures and infrastructure in cities and communities throughout the world. The carbon dioxide emissions from the cement production represent a large portion of the embodied carbon in these structures (Meggers et al., 2012; Omar et al., 2014). There are various opportunities to reduce this embodied carbon in concrete from the production of cement such as reduced energy usage and partial substitution of the cement with supplementary cementitious materials (Huntzinger & Eatmon, 2009; Xu et al., 2013).

However, a significant portion of the carbon dioxide produced can be re-absorbed by the concrete in the reverse reaction to calcination, commonly referred to as carbonation (Pade & Guimaraes, 2007). The carbonation process is generally very slow, taking years if not decades to reach significant levels for many concrete applications. Carbonation in primary applications of concrete can be a concern if high levels of carbon dioxide sequestration evidenced by a pH drop reach reinforcing bars, possibly enhancing corrosion (Mehta & Monteiro, 1993; Neville, 1981). However, there is interest in accelerating this process for appropriate primary life applications of concrete, and for secondary usages of recycled concrete aggregate in order to make the life cycle of concrete structures more carbon neutral with respect to the calcination reaction.

1.1. Concrete carbonation and carbon dioxide exposure in ambient air

The carbonation process is frequently modeled as carbon dioxide dissolving in water and then reacting with the portlandite (calcium hydroxide) within cement paste to form calcite (calcium carbonate). Eqs. (1)–(3) represent chemical equilibriums in a typical aqueous (aq) carbonate system:

$$CO_2(g) + H_2O(l) = H_2CO_3(aq) \tag{1}$$

$$H_2CO_3(aq) = H^+(aq) + HCO_3^-(aq), \ pKa = 6.35 \tag{2}$$

$$HCO_3^-(aq) = H^+(aq) + CO_3^{2-}(aq), \ pKa = 10.33 \tag{3}$$

Eq. (1) represents dissolution of gaseous (g) carbon dioxide into water and the equilibrium is typically represented by Henry's Law (Snoeyink & Jenkins, 1980). In the water solution the dissolved

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carbon dioxide can then further dissociate into bicarbonate and carbonate ions with the equilibrium constants given by the noted pKa (equilibrium constant) values for dilute aqueous systems. Water in concrete pores may be much more concentrated, but these pKa values still provide relative information.

The higher pH of pore water in uncarbonated cement paste is usually caused by the dissociation of solid (s) calcium hydroxide, a major component of hydrated cement, which can then react as in the following chemical reactions of the carbonation process:

$$Ca(OH)_2(s) = Ca^{2+}(aq) + 2OH^-(aq) \tag{4}$$

$$Ca^{2+}(aq) + CO_3{}^{2-}(aq) = CaCO_3(s) \tag{5}$$
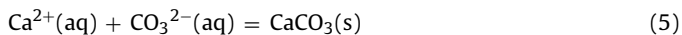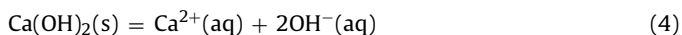
The reactions in Eqs. (1)–(5) continue over time with the addition of carbon dioxide from the environment, allowing more calcium carbonate to form until theoretically all of the calcium hydroxide could be converted to calcium carbonate, although this has not been seen to happen to full conversion in concrete applications for typical use over typical lifetimes (Engelsen et al., 2005).

Cement carbonation in concrete structures has been widely studied for many decades, and is usually a very slow process, with significant carbonation on outer surfaces, and a *carbonation front*, slowly progressing inward at typically decreasing rates of millimeters or less annually. The *rate of carbonation* commonly refers to the rate of progression of this carbonation front and the depth of this front of carbonation (D_c) and is traditionally modeled as a function of the square root of time (t) as in Eq. (6), where k_c is the carbonation front coefficient.

$$D_c = k_c * t^{(1/2)} \tag{6}$$

According to researchers of traditional concrete carbonation such as in buildings, k_c increases at optimum ambient air relative humidities (50–60%), and with higher temperatures, higher partial pressures of carbon dioxide, higher porosities, larger surface areas, and higher pozzolan material contents (Banks & Macabe, 1988; Engelsen et al., 2005; Park & Tia, 2003).

Engelsen et al. (2005) indicates that concrete saturated with water due to a 100% relative humidity under ambient air conditions carbonates more slowly than unsaturated concrete. It is theorized that in traditional concrete applications exposed to ambient air, water from a high relative humidity may block the micro pores common in the cement paste. This may then limit the rate of carbonation by reducing the surface area available for the dissolution of carbon dioxide from the air in the water filled micro pores areas at the ends of the saturated pores.

Conversely, if the relative humidity is too low, water will not be available in the shallow pores for calcium hydroxide to dissolve and little to no carbonation will occur. The theorized optimum *carbonation rate* based on relative humidity of typical concrete structures such as buildings exposed to ambient air has some water in the micro pores, but not enough for saturation.

The primary method for identifying carbonation depth in concrete is by using a pH indicator. The carbonation depth is frequently defined by industry as the depth at which a phenolphthalein indicator turns from red to colorless. A pH indicator, such as phenolphthalein, can be used because the pH decreases with carbonation due to the shift from calcium hydroxide dominance to calcium carbonate dominance (Chang & Chen, 2006; Lagerblad, 2007; Pade & Guimaraes, 2007).

1.2. Pervious concrete and carbonation

Pervious concrete is a type of concrete with larger interconnected pores in addition to the typical cement paste micro pores. It is used for pavements and other structures where it is beneficial for water to be able to flow through. In pervious concrete,

carbonation cannot be determined by depth from its outer surface because of the influence of its extensive interconnected pore structure, which allows ambient air and water to more readily reach interior spaces. When water flows through pervious concrete, the pH of the water will change due to the presence of calcium hydroxide and calcium carbonate in the cement paste, with lower pH values indicating more calcium carbonate, or a higher amount of carbonation. Therefore, the pH of the exfiltrate from pervious concrete may be a relative indicator of the amount of carbonation in the pavement over time.

Several previous studies on pervious concrete include information on the pH of water exfiltrated through pervious concrete. Thomle and Haselbach (2011) specifically focused on the declining pH of waters exfiltrated through pervious concrete exposed to ambient air over time. The lower pH of the more carbonated pavement is typically a preferred condition if exfiltrate from the pavement might discharge to natural waters where the aquatic life is sensitive to high pH. They found that pH decreased with time and that the pH of the exfiltrate from specimens with more outer surfaces exposed to ambient air lowered more rapidly than those with fewer exposed outer surfaces, an indication of increased carbonation with increased exposure to carbon dioxide in the ambient air. Park and Tia (2003) evaluated the pH of laboratory prepared pervious concrete samples that were immersed in river water in order to study contamination from concrete alkalinity. Park and Tia (2003) reported that the pH had dropped from 10.6 to 8.7 in 90 days as their specimens soaked in river water, but no explanation was given for the drop. Several other studies did not focus on pH or carbonation but provided some pH information of either pervious concrete or pervious concrete pavement systems, where the pavement systems include an underlying aggregate storage bed for stormwater management (Collins, 2007; Horst et al., 2008; Kwiatkowski et al., 2007; Luck et al., 2008).

Cylindrical pervious concrete samples which were exposed to ambient air on both ends in the Thomle and Haselbach (2011) study decreased on average to a pH less than 10 based on a thirty minute immersion test in approximately a half year, and to a pH of approximately 9 in under a year. This study focused on pervious concrete independent of other materials in the pervious concrete system such as granular base material and sub-base material. Thomle and Haselbach (2011) focused on rate limiting conditions for carbonation, namely the low relative humidity of the semi-arid climate in the laboratory, and the samples were periodically inundated with de-ionized or tap water, representative of precipitation events with fairly clean rainwater.

The Park and Tia (2003) study indicated that this decline in pH took only a few months when submerged in river water. This is contrary to the accepted carbonation rate theories of traditional concrete exposed to ambient air, where saturation due to high relative humidities decreased the rate of carbonation. However, river waters may contain substantial amounts of carbonate species, generally in the form of bicarbonates (Stumm & Morgan, 1996), which may have contributed to the carbonation process. This leads to the hypothesis postulated herein that concrete submerged in carbonate species laden waters may carbonate at a faster rate than concrete exposed to ambient air and that this rate may be through a modified mechanism from the aforementioned models.

The carbonate and bicarbonate levels in the Park and Tia (2003) study were not given. However, river water generally has concentrations of bicarbonate anions from 20 mg/L to 250 mg/L (Stumm & Morgan, 1996). In traditional concrete, carbonate species are thought to diffuse more slowly into pores than carbon dioxide because carbonate species are larger molecules (Lagerblad, 2007). However, with a higher concentration gradient caused by the additional carbonate species in the river water, the specimens may have carbonated at a higher rate than ambient air carbonation.