



Leaching of ANC and Chromium from Concrete: Effect of Aging Simulated by Sample Carbonation

S. Demars · G. Benoit

Received: 15 March 2019 / Accepted: 23 June 2019 / Published online: 2 July 2019
© Springer Nature Switzerland AG 2019

Abstract Chemicals leached from concrete are an important way that urban stormwater can influence water quality. In this study, we evaluated the weathering properties of sidewalk samples and tested how carbonation (exposure to elevated levels of gaseous CO_2) can be used to simulate natural aging of concrete. The experiments focused on acid neutralizing capacity (ANC), which is known to be released by concrete in large amounts, and Cr(VI), because of its established carcinogenicity and prevalence in concrete. Chemical weathering of crushed sidewalk samples was measured with upflow recirculating columns carrying simulated acid rain. The weathering rate of ANC from four different samples was found to decrease after 1 week of exposure to a 5% carbon dioxide atmosphere and to remain constant thereafter through 8 weeks of carbonation treatment. In contrast, weathering of chromium (VI) *increased* after exposure to a 5% carbon dioxide atmosphere for 1 week, though it also remained stable from then through 8 weeks of carbonation. Almost all ions approached steady state after 2.5 h in the recirculation columns irrespective of carbonation time. The main contributor of ANC was Ca^{2+} ion, though this was partly balanced by an unexpectedly high amount of SO_4^{2-} . A notable exception to the temporal leaching pattern was largely un-ionized Si, which continued to increase in concentration for at least 3 days of recirculation. Si

levels were also higher than is generally observed for aluminosilicate weathering in small watersheds, a novel finding.

Keywords Concrete · Leaching · Acid neutralizing capacity · Chromium · Urban watersheds

1 Introduction

Concrete is a major construction material for the urban built environment, comprising roadways, parking lots, sidewalks, buildings, and water drainage pipes. Concrete building materials contain calcium hydroxide and calcium carbonate, both of which weather to release acid neutralizing capacity (ANC) into the environment. ANC, also known as alkalinity, is a naturally occurring property of water and reflects its capacity to resist pH change on introduction of strong acids or bases. It can be quantified in terms of either the excess of strong bases over strong acids (as reflected by their counter ions, Ca^{2+} , Mg^{2+} , Na^+ , K^+ minus Cl^- , SO_4^{2-} , and NO_3^-) or the amount of weak acid anions (mainly carbonates) that must be titrated to reach the CO_2 equivalence point.

Weathering of concrete, and release of ANC, can be viewed as beneficial insofar as it makes downstream aquatic systems more resistant to stressors like acid rain. On the other hand, it alters background chemistry, making soft water systems harder, potentially changing natural species consortia. Furthermore, hexavalent chromium ($\text{Cr}[\text{+VI}]$), a toxic carcinogen, is also weathered into the environment from concrete if the raw materials used

S. Demars · G. Benoit (✉)
Yale School of Forestry and Environmental Studies, 195 Prospect St., New Haven, CT 06511, USA
e-mail: gabouryb@gmail.com

in its manufacture contained this metal, as is often the case. This hazard led the European commission to restrict chromium in cement raw materials to below 2 ppm soluble Cr[+VI] (Hills and Johansen 2007), although chromium is not currently restricted in cement raw materials in the USA.

1.1 ANC Leaching from Concrete

An original contribution of the current research is a set of experiments detailing ANC weathering from concrete in continuous flow columns. Studies of this kind have been performed on concrete slabs under continuous flow conditions (Schiopu et al. 2009) and on concrete gravel by means of batch leaching tests (Engelsen et al. 2009), but not in columns, which are more easily reproduced. Many relevant studies on the effects of concrete impervious cover are observational studies, which are summarized below.

ANC export from watersheds has been proposed as an indicator of urban landcover, although its use in this way is not common. Williams et al. (2005) investigated river solutes in the Ipswich river basin in northeastern Massachusetts by means of regression analysis. They found ANC to be highly correlated with urban land cover, with ANC exhibiting a similar temporal pattern to Ca^{2+} concentration. They suggested that the solutes are associated through weathering of CaCO_3 in urban concrete or agricultural lime. Baker et al. (2008) reported a strong association of dissolved inorganic carbon (DIC) with urban watersheds in northern and southern England, with urbanized catchments yielding DIC values generally higher even than catchments underlain with carbonate bedrock. They suggested that riverine DIC concentrations are influenced by urban land cover above a critical areal threshold of approximately 5%. Also, Herlihy et al. (1998) found that ANC, chloride, nutrients, and base cations were strongly correlated with urban and agricultural land cover of watersheds in the mid-Atlantic region, though they did not draw a connection between ANC and concrete.

1.2 Cement Production and Chromium

Concrete is a combination of aggregate (sand and gravel filler and the like) and ordinary Portland cement or OPC. This material is a dry powder produced from ground gypsum and clinker. Clinker is made by heating a limestone and clay paste mixture to 1450 °C in a

rotating kiln and is composed of limestone and aluminosilicate minerals, and sometimes, small amounts of iron oxides can also be added (Bodaghpour et al. 2012; Chen et al. 2009).

Hazardous wastes are commonly co-incinerated in cement kilns as fuel or raw material. The high temperature of the furnace creates an oxidizing environment, which incorporates ash and slag into the clinker (Espinosa and Tenório 2000). The high heat also oxidizes Cr^{3+} in raw materials fed into cement kilns to Cr(+IV), Cr(+4.6), Cr(+V), and Cr(+VI) forms (Sinyoung et al. 2011a, b). In the solid phase, Cr(+VI) is found primarily in the form of chromates, such as calcium chromates and aluminum chromates, which are toxic, soluble, and common in manufactured cement (Hills and Johansen 2007; Leisinger et al. 2014; Sinyoung et al. 2011b). Due to the ubiquity of Cr(VI) in cement, and a European Union directive prohibiting sale of cement containing more than 2 ppm soluble Cr(VI), reducing materials are used in Europe to minimize the level of leachable Cr(VI) formed in cement production, maintaining it at lower, less hazardous, oxidation states (Bodaghpour et al. 2012; Hills and Johansen 2007).

1.3 Chromium Solubility from Concrete

Chromate (Cr [VI]) is soluble in water above pH 8, a level which is common in urban stormwater (McNeill et al. 2011). Wang and Vipulanadan (2000) tested the leaching of K_2CrO_4 encased in cement. XRD analysis showed that Cr was in the form of CaCrO_4 and was found to account for most of the chromium detected in a total chromium analysis, confirming that most of the leached chromium was in the Cr(VI) form. Sinyoung et al. (2011b) reported a linear relationship between initial solid chromate concentration in cement and leached concentrations of total chromium. Cr(VI) was 80–90% of total chromium in these experiments, confirming its solubility relative to other chromium oxidation states.

1.4 Concrete Aging

Concrete alters chemically as it ages after initial emplacement. In particular, calcium hydroxide reacts with atmospheric carbon dioxide and slowly converts to calcium carbonate during the service life of concrete and these two minerals weather dissimilarly. Predicting the extent of ANC and Cr weathering from concrete and

their subsequent impact on downstream ecosystems requires a better understanding of how its properties change over time. However, experiments that are long enough to simulate the expected service life of concrete structures are impractical. The alternative, to test a chronosequence of concretes emplaced at various times, fails because processing the naturally aged materials exposes fresh surfaces unlike those found in the field.

Accelerated carbonation of cement, i.e. intentional exposure to elevated levels of gaseous CO₂, is used to simulate the aging process that concrete undergoes in the several years following its installation (Groves et al. 1990; Hyvert et al. 2010; Neves et al. 2013). ANC and chromium are known to be leached from concrete in relatively large amounts, yet little is known about their chemical behavior in cement, particularly their release following cement carbonation, which may alter their leaching. Previous studies (Müllauer et al. 2012; Van Gerven et al. 2006) used batch experiments with freshly cured concrete blocks subjected to accelerated carbonation to evaluate its influence on the leaching properties of cement-bound waste, particularly fly ash. This differs from the current study, which collected concrete from representative outdoor sidewalks, granulated them for lab analyses, and subjected them to accelerated carbonation, followed by exposure to simulated acid rain in recirculation experiments (Müllauer et al. 2012; Van Gerven et al. 2006). Müllauer et al. (2012) found that carbonation increased the chromium leaching rate of cement by up to a factor of 8 during batch tests.

In this study, we investigated the weathering response of concrete samples exposed to an enriched carbon dioxide atmosphere, which has been used to accelerate and simulate natural aging in the environment. Specifically, the effect of conversion of calcium hydroxide by CO₂ to calcium carbonate on weathering of ANC and Cr(VI) was examined.

2 Experimental Methods

2.1 Review of Previous Experimental Methods

Apparatuses used to test calcite and cement dissolution rates have differed across research groups, whose designs varied to address specific research questions. Experiments conducted in the current study were designed to attempt to predict and explain results from field studies (reported elsewhere), whereas other

investigators addressed different applied questions, which included nuclear waste solidification/stabilization modeling (Dayal and Reardon 1994), chromium leaching from un-aged cement (Kayhanian et al. 2009), evaluation of oil well casings to be used for CO₂ sequestration sites (Duguid and Scherer 2010), SO₂ removal efficiency from combustion exhaust via CaCO₃ (Lancia et al. 1997), and studies of aquifer dynamics (Rauch and White 1977). Also, most studies of concrete leaching focused on the effects of aqueous solutions on concrete, while this study focused on the effect of concrete on aqueous solutions.

Earlier experimental apparatuses included ambient pressure flow-through columns (Dayal and Reardon 1994; Duguid and Scherer 2010; Kayhanian et al. 2009; Lancia et al. 1997; Rauch and White 1977), recirculating apparatuses (Duguid and Scherer 2010; Rauch and White 1977), high pressure flow-through columns (Luquot et al. 2013; Noiriel et al. 2009), stirred batch reactors (Arakaki and Mucci 1995; Busenberg and Plummer 1982; Dreybrodt et al. 1996; Eisenlohr et al. 1999; Pepe 2001; Plummer and Wigley 1976; Plummer et al. 1978), bottle batch reactors (Eisenlohr et al. 1999; Reardon and Fagan 2000), and pH stat reactors (Brogren and Karlsson 1997; Suarez 1983; Ukawa et al. 1993). Of the many experimental apparatus design types above, ambient pressure recirculating column apparatuses are most suitable for the experiments we performed to simulate concrete runoff in the built environment. The two studies using this type of apparatus and their characteristics are included in Table 1. Ambient pressure recirculating columns are most suited to the experiments we performed because they most closely match pressure, flow, and contact conditions the runoff encounters during exposure to concrete surfaces in the built environment. Furthermore, compared to batch reactors, they allowed us greater control in simulating the hydrodynamic conditions that occur in the field. In particular, the columns enabled us to more reliably control flow velocities and thereby diffusive boundary layer thicknesses.

2.2 Concrete Sources, Processing, Treatment, and Composition

Four concrete samples were collected from the field and designated C1–C4. Samples C1 and C2 were scrap concrete from sidewalks in New Haven, Connecticut. These were received from sidewalk sections in service for at least a year and removed during tree planting by

Table 1 Characteristics of published studies using ambient pressure, flow-through columns for weathering tests of cement, concrete, and calcite

Publication	Apparatus type	Solid type	Leachate	Leachate volume	Flow rate	CO ₂ regulation	Run time
Dayal and Reardon (1994)	Flow-through	Freshly cured ¹⁴ C-doped cement	Deionized water	160 mL	2.4–22.7 mL/h	Ambient pCO ₂ in closed system	240 days
Duguid and Scherer (2010)	Recirculating	Freshly cured cement or concrete	0.5 M NaCl brine	210 l	8.3–8.7 mL/min	CO ₂ saturation	31 days
Kayhanian et al. (2009)	Flow-through	Aggregate or freshly cured concrete	DI acidified with nitric acid to pH 7, 6, 5, 4	30 l	0.63 L/h	Ambient pCO ₂ in open system	8 h
Lancia et al. (1997)	Flow-through	0.2–3 mm diameter ground limestone	SO ₂ , HCl, or H ₂ SO ₄ acidified DI	12 mL (column vol.)	0.78–3.42 L/min	Ambient pCO ₂ in closed system	6 h
Rauch and White (1977)	Recirculating	Calcite and other natural geologic samples	Deionized water	3.5 L	550 mL/min	CO ₂ saturation	5 days

the Urban Resources Initiative (URI) of the Yale School of Forestry and Environmental Studies. Samples C3 and C4 were sidewalk concrete from removal and construction in New York City, NY, at 89 Bleecker Street. These samples were photographed and weighed and their composition determined via ion microprobe analysis (Table 2).

Concrete samples were processed to yield gravel-sized fragments of 4.00–4.75 mm diameter. First, the bulk concrete samples were cut to 30-cm lengths on a water-cooled automatic diamond table saw. Then, these lengths were broken into golf ball sized pieces with a screw wedge apparatus, and these fragments were fed into a chipmunk crusher to yield coarse concrete gravel of heterogeneous size. The coarse concrete gravel was fed into a mill to yield fine gravel with pebble sizes near the target 4–5-mm-diameter range. The milled concrete gravel was then sieved successively, with number 4 (4.76 mm) and 5 (4.00 mm) sieves. The concrete gravel samples were rinsed three times with deionized water and dried overnight at 60 °C. Each fragment of the resulting concrete gravel is estimated to have a macroscopic surface area of 60 mm² based on an assumed spherical shape (John et al. 1998; Plummer et al. 1978).

Table 2 Concrete sample composition measured by electron microprobe as percentages of total detected elements

	C1 composition (%)	C2 composition (%)	C3 composition (%)	C4 composition (%)
O	55	51	48	56
Ca	19	23	28	17
C	13	9.9	8.4	14
Si	8.3	9.0	8.6	6.0
Al	2.0	2.2	1.5	1.9
Mg	1.2	2.3	1.7	1.5
Fe	0.76	2.0	1.5	1.7
S	0.21	0.24	0.49	0.30
Cl	0.051	0.10	0.74	0.15
K	0.13	0.20	0.29	0.18
Na	0.078	0.072	0.35	0.081
F	0.30	0.072	0.12	n.d.
Ti	0.065	0.15	0.091	0.081
P	0.061	0.14	0.068	0.11
H	n.d.	n.d.	0.14	n.d.
Mn	0.021	0.032	0.021	0.081
Ni	0.010	0.016	0.018	n.d.

Obtaining a more detailed analysis of surface area was rejected because the surfaces are expected to change morphology in the course of the experiments, generally becoming smoother at a microscopic scale. As a consequence, a detailed microscopic surface area determination (e.g., by BET analysis) seemed unwarranted.

Slides of the concrete samples were prepared and polished for electron microprobe analysis of their elemental composition (Table 2). First, bulk concrete samples were sliced into 4 mm thick plates on a water-cooled enclosed automatic diamond table saw. The resulting rectangular concrete chips were labeled and polished on an 18-in.-diameter lap grinder using progressively finer sandpaper. The polished chip was then heated and coated with Petropoxy 154 to produce a smooth surface.

The exposed concrete surface on slides to be prepared for electron microprobe analysis were made thinner on a diamond grinder until the sample was about 2-mm thick. The exposed concrete surface was then polished on an 18-in.-diameter lap grinder with progressively finer sandpaper before the samples were analyzed on an electron microprobe. Concrete samples mounted to slides for visual microscopy were made thinner on a diamond grinder until the slide was translucent. The exposed concrete surface was then polished on an 18-in.-diameter lap grinder with progressively finer sandpaper.

Concrete slides were coated with conductive carbon and analyzed semi-quantitatively via electron dispersive spectroscopy on a JEOL JXA-8530 electron microprobe analyzer. A beam size of 20 μm was used with a beam intensity of 10 nA and voltage of 15 kV. Dwell times were 20 ms for F, Na_2O , MgO, Al_2O_3 , SiO_2 , TiO_2 , Cr_2O_3 , FeO, P_2O_5 , Cl, and NiO; 40 ms for MnO, SO_3 , and K_2O ; and 140 ms for CO_2 . Chromium was also measured by acid dissolution of concrete samples followed by ICP-AES analysis of the solution, because electron microprobe detection limits were inadequate for analysis of Cr in the concrete samples. Seven microprobe measurements were taken for slides C1, C2, and C4 and 40 measurements for slide C3 in a lateral transect of cementitious material, avoiding aggregate. Results were reported as weight percent (Table 2). Backscattered electron images were also taken of the concrete samples (Fig. 1).

2.3 Testing the Exposure of Concrete Materials to an Enriched 5% Carbon Dioxide Atmosphere

Experiments were performed on the crushed samples to test the effect of exposure of concrete

materials to an enriched 5% carbon dioxide atmosphere on the amount and nature of compounds released from concrete materials after 1, 2, 3, and 8 weeks of contact. Samples of crushed, sorted concrete were placed into a chamber with a 5% carbon dioxide atmosphere and 50% relative humidity to accelerate chemical aging. Atmospheric composition was held constant during the tests via an automated system that maintained conditions within $\pm 3\%$ of the target values (0.0015% absolute). The accelerated aging of concrete proceeds by absorption of carbon dioxide, which converts calcium hydroxide to calcium carbonate (Hyvert et al. 2010; Pu et al. 2012).

Portions of approximately 25 g of each concrete sample, C1–C4, were added to the 5% carbon dioxide chamber. One lot of each concrete sample type was removed from the chamber after 1, 2, 3, and 8 weeks in addition to one measured at time 0. Samples collected from the carbon dioxide chamber and a non-carbonated control were loaded into 2-cm-diameter LDPE columns which were inserted into an up flow recirculating apparatus (Fig. 2). As described earlier, recirculation simulates exposure of concrete to acid rain, which generally occurs over a period of a few hours as it contacts buildings, flows across impervious surfaces, and travels through pipes. The apparatus contained a lab-prepared solution designed to simulate local acid rain, and consisting of 0.013 mM nitric acid and 0.010 mM sulfuric acid, based on the average concentrations of NO_3^- and SO_4^{2-} in rainfall recorded near New Haven, CT in 2009 (National Atmospheric Deposition Program 2010).

2.4 Upflow Reactor Conditions

The reactor (Fig. 2) contained 1300 mL of simulated acid rain, and a blank was taken and its volume was replaced before starting the experiment and adjusting the column flow rate to 210 mL/min. For each carbonation exposure time interval, 7.5-mL samples were collected after 0.0, 0.25, 0.5, 1.0, 1.5, 2.0, and 2.5 h of recirculation. Major ions were determined on collected samples. A 125-mL sample was also collected at the 2.5-h interval for titrated ANC analysis to compare to values calculated from strong base cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) via ICP-AES minus strong acid anions (Cl^- , NO_3^- , and SO_4^{2-}) via ion chromatography for quality control. Cr(VI) was measured by ICP-AES. On select samples, the Cr(VI) species was measured by the

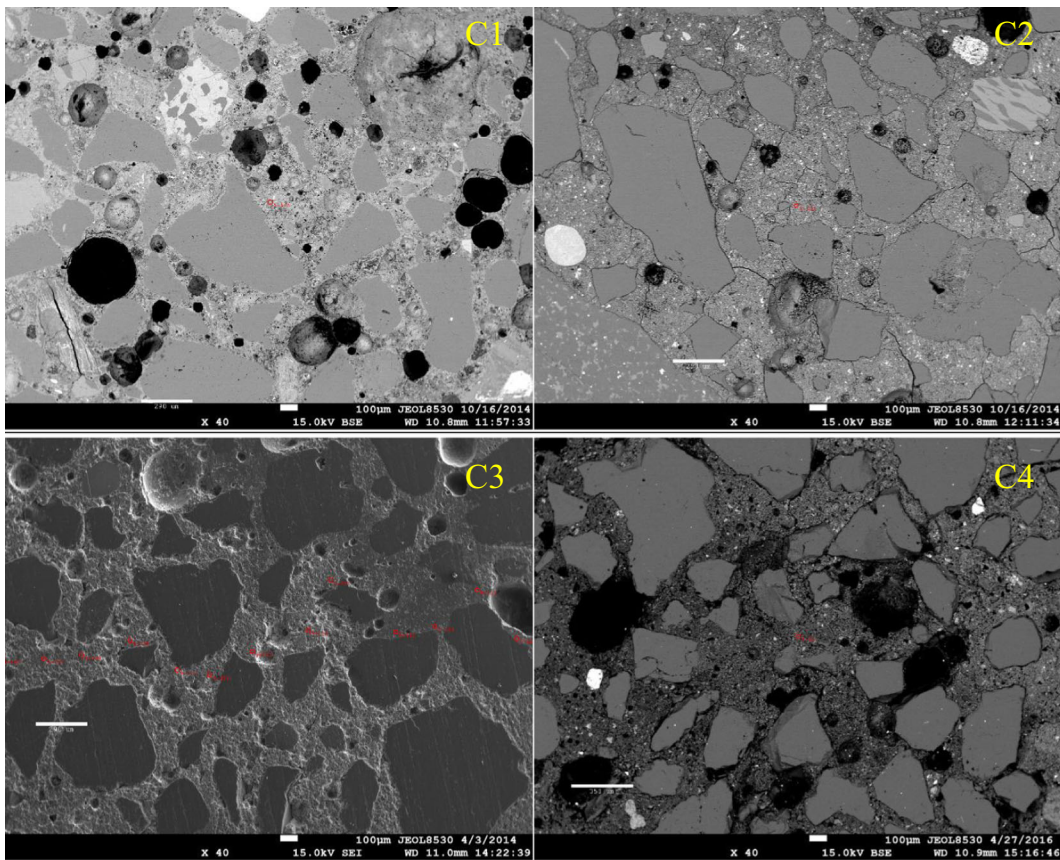
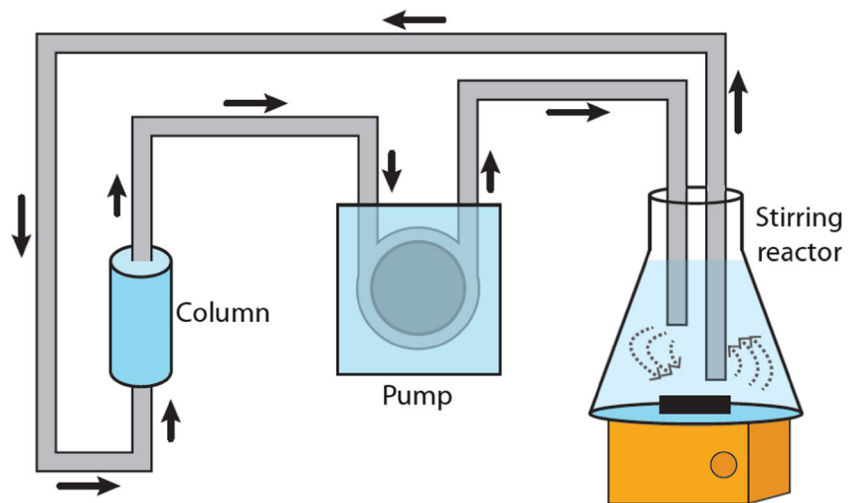


Fig. 1 Electron micrographs of concrete samples shown clockwise as C1, C2, C3, and C4. Concrete samples display similar aggregate mineral size and distribution. They also have similar pore size distribution and aggregate-to-cement ratios

diphenylcarbazide colorimetric method (Standard Method 3500-Cr D.), which showed that Cr(III), by difference, was a negligible fraction in our samples.

Exchange of substances between solution and the solid concrete can be either reaction limited or transport limited. The former is a function of the rate of the

Fig. 2 Recirculating column experimental apparatus diagram. The stirring reactor allows equilibration with atmospheric CO₂, as is expected in the field



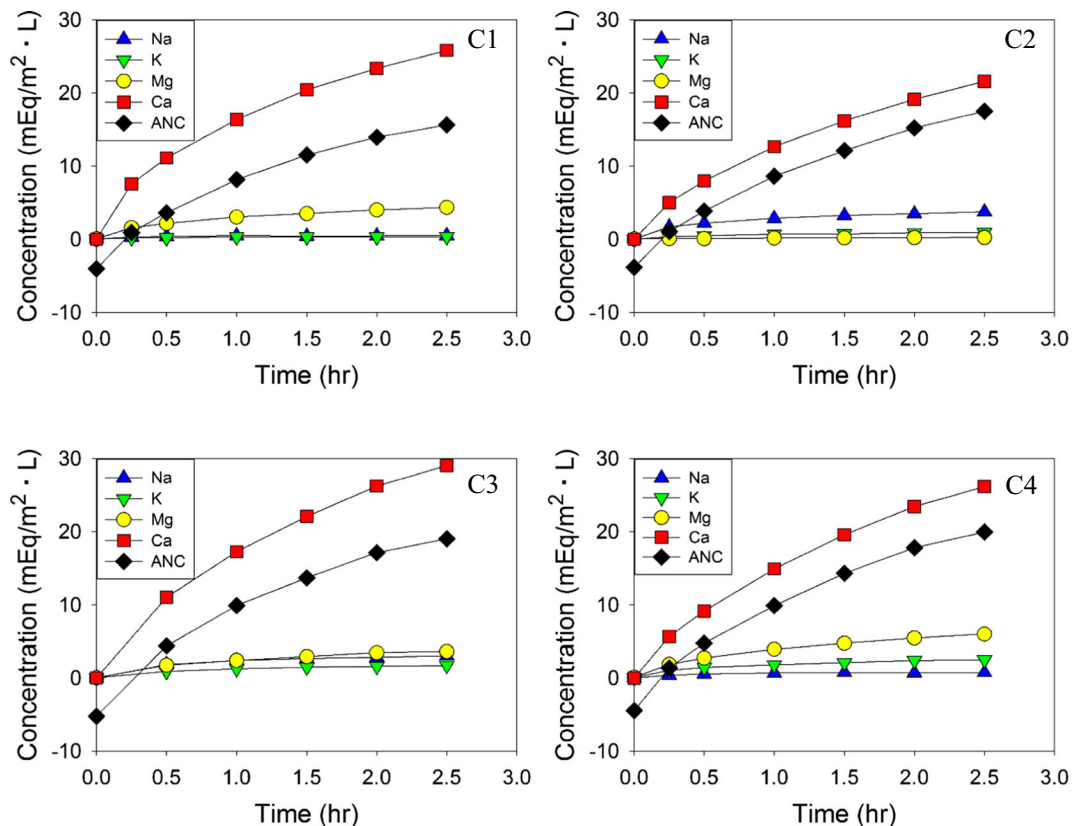


Fig. 3 Cation and ANC concentrations as a function of time during recirculating column experiments on concrete samples C1, C2, C3, and C4 treated with 8 weeks of exposure to a 5%

CO₂-enriched atmosphere. Concentrations have been multiplied by 70 to reflect the volume:surface ratio used in our experiment

specific chemical reaction, and the latter is determined by physical factors, especially (1) the diffusive boundary layer (DBL) thickness, and (2) the difference between the concentrations immediately at the interface and in bulk solution. If the system is transport limited, then leaching will vary with flow rate, which changes the DBL thickness ($DBL \propto \text{Velocity}^{-1/2}$). Judging from first principle calculations based on Fick's first law of diffusion, we believe that leaching is reaction limited in the field, and we wanted our experiments to match this condition. Our selected volumetric flow rate, combined with column and fragment geometry, yields a flow velocity (2.2 cm/s) in our tests, similar to what occurs in the field as sheet or shallow open channel flow across concrete surfaces. For comparison, ordinary concrete with a slope of 1% would have flow velocity near 5 cm/s for a water depth of 1 mm based on Manning's formula. Clearly, the Manning formula is only approximate under these conditions, but it matches simple dye tracer experiments we conducted at field sites. Perhaps

more importantly, we investigated variations in flow rate in our apparatus and found that changes in leaching did not have the inverse square root dependence on velocity that would indicate transport limitation, supporting our belief that the systems were reaction limited.

To contextualize our measurements, water spent approximately 3 s in contact with concrete granules during each pass through the apparatus. Recirculation took approximately 6 min, so contact time amounted to 30 s for each hour of operation. Thus, steady-state concentrations, which took about 3 h to achieve, occurred after about 90 s of total contact time.

Based on a count of the number of fragments used for each concrete, and the macroscopic area calculated as described earlier, we estimate that each experiment involved approximately 0.014 m² of exposed surface area. For an urban locale with 50% imperviousness of which 10% is concrete materials, the ratio of surface area to water volume of a 2 cm storm would be 10:1. This can

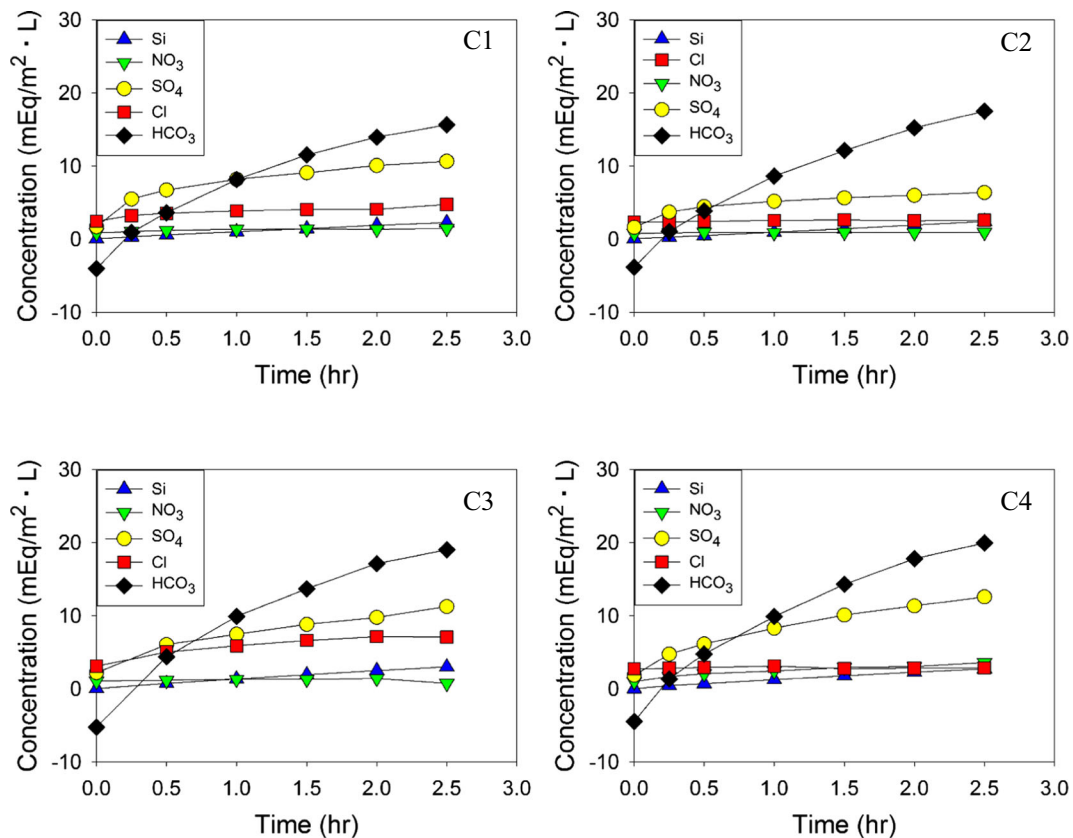


Fig. 4 Anion concentrations as a function of time during recirculating column experiments on concrete samples C1, C2, C3, and C4 treated with 8 weeks of exposure to a 5% CO₂-enriched atmosphere. Concentrations have been multiplied by 70

be compared to a ratio of about 70:1 ($[0.014 \text{ m}^2]^{-1}$) in our laboratory experiments, indicating that they were a reasonable order-of-magnitude approximation of field conditions.

Note that we use this same multiplier (70) to express concentrations in Figs. 3, 4, and 5 to normalize results to surface area used in our experiments. Raw concentrations can be obtained by dividing results by that same number.

2.5 QA/QC Data for ANC and Cr(VI) Analyses

The average difference between ANC values measured via titration to the CO₂ equivalence point and charge balance was -7.0% , and average closure of charge balance was -1.75% . This supports the validity of our charge balance ANC data. The average instrumental uncertainty between measured ANC check standards and their certified values was -0.28% , with a relative

to reflect the volume:surface ratio used in our experiment. HCO₃⁻ values were obtained from difference by electroneutrality, so they are negative at time 0. It reflects initially elevated H⁺, and this anomaly disappears at later time intervals

standard deviation of 0.34% for the check standard measurements. This confirms the precision of our instrumental methods for ANC. The average instrumental uncertainty of measured Cr(VI) check standards compared to their certified values was 9.0% , with a relative standard deviation of 6.5% for the check standard measurements. This confirms the precision of our instrumental methods for Cr(VI).

3 Results and Discussion

3.1 ANC and Major Ions

In most cases, weathering of ions approached maximal levels within the first hour of exposure to simulated acid rain in our recirculating reactors (Figs. 3 and 4). For all four concretes, Ca²⁺ and SO₄²⁻ were the main strong base cation and strong acid anion released, though

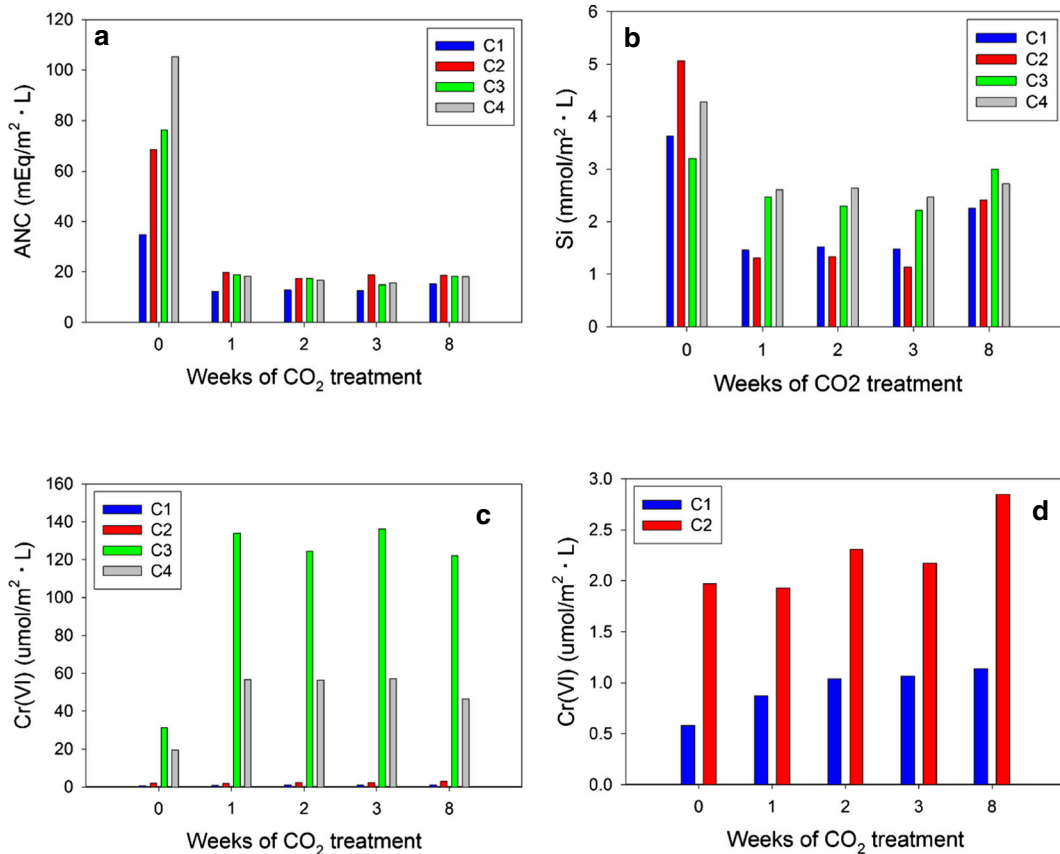


Fig. 5 Area-normalized concentrations for ANC (a), Si (b), and Cr (c, d) on concrete samples C1, C2, C3, and C4 treated with increasing exposure time to a 5% CO₂ atmosphere. Results are for 2.5 h recirculating experiments, selected to match typical exposure

times of water to concrete in the field. Concentrations have been multiplied by 70 to reflect the volume:surface ratio used in our experiment

HCO₃⁻ was released more rapidly and eventually became the principal anion. Both calcium and sulfate continued to increase beyond the first hour, but were beginning to plateau by 2.5 h. The difference between these two is close to the increase in ANC, as the other strong acid and base cations were much lower, except for Cl⁻ in some cases. These results suggest that weathering of ANC from concrete is relatively insensitive to the length of time that water is exposed to the surfaces beyond the first few hours, a condition which could facilitate scaling from lab to plot scale measurements (manuscript in preparation).

The relatively high amount of sulfate as a counterion is somewhat surprising and has not been noted previously. Attack on concrete by sulfate-rich solutions is well known and widely studied (e.g., Wang 1994), but its importance as a component of concrete leachate is a novel observation. Among other things, a high sulfate level means ANC leaching is not as great compared to

calcium as it would be if bicarbonate were the counterion.

Final ANC (defined here as values after 2.5 h of recirculation) differed across the four concretes for freshly ground (uncarbonated) samples (Fig. 5), varying from 500 to 1500 μeq/L. These values are high compared to unpolluted surface waters in the New Haven region, which are typically less than 100 μeq/L in headwater streams and close to 200 μeq/L in undeveloped watersheds. They are comparable to local surface waters in heavily urbanized watersheds, which can have values approaching 700 μeq/L.

Following just a single week of carbonation, ANC concentrations after 2.5 h in the weathering experiment apparatuses were lower than for trials with freshly ground, uncarbonated concrete (Fig. 5). Levels declined by roughly a factor of two, though results varied among the concretes. Following the first week of concrete carbonation treatment, final ANC levels were stable

for concrete gravel exposed to elevated CO₂ for 1 through 8 weeks. Samples C1, C2, C3, and C4 had relative standard deviations of 9.7, 5.0, 10.1, and 7.2%, respectively, across 1 through 8 weeks of carbonation treatment, compared to initial drops of 64 to 83% between weeks 0 and 1, indicating stable conditions had been achieved after 1 week. After carbonation, the samples were also more similar to each other in final ANC levels than before. These results suggest that a standard value of 18 mEq/m² L can be used for any aged concrete when evaluating its potential influence on ANC. This value would then need to take into account the water:concrete ratio of the system under evaluation. For the urban locale described earlier, 1 m² of concrete would interact with 100 L of water and thus receive an increment of roughly 180 µeq/L.

The quick drop in ANC weathering rate after a single week of carbonation treatment was unexpected but means that lab experiments to evaluate ANC weathering rates can be conducted after a relatively short period of sample pretreatment to compensate for exposure of fresh surfaces during initial sample processing.

3.2 Cr(VI)

Cr levels on freshly ground (and uncarbonated) concretes also differed among samples. The range was more marked than for ANC, varying from 0.58 to 31 µmol/m² L (corrected for area) for week 0. In contrast to ANC, final Cr(VI) concentrations in the weathering experiments increased following concrete carbonation and recirculation treatment, though only for two of the four samples. For these two (C3 and C4), leached Cr doubled at least, whereas for C1 and C2, Cr remained low. This meant that the total range of Cr also increased dramatically, with a range of almost a factor of 100 between the lowest and highest samples. Curiously, this cannot be explained simply by the composition of the concretes. As the highest chromium measured by microprobe analysis was below the detection limit, we reanalyzed by leaching the samples with strong acid and measuring by ICP-AES. The results indicate that sample C3 had the highest Cr content, whereas C1 and C4 had intermediate levels, and C2 was the lowest. All values were considerably higher than the European limit of 2 ppm (e.g., 16 ppm in C1, 6 ppm in C2, 43 ppm in C3, and 13 ppm in C4). It may be that leachable Cr depends in part on the

oxidation state of the Cr, with Cr(+VI) known to be more leachable than Cr(+III).

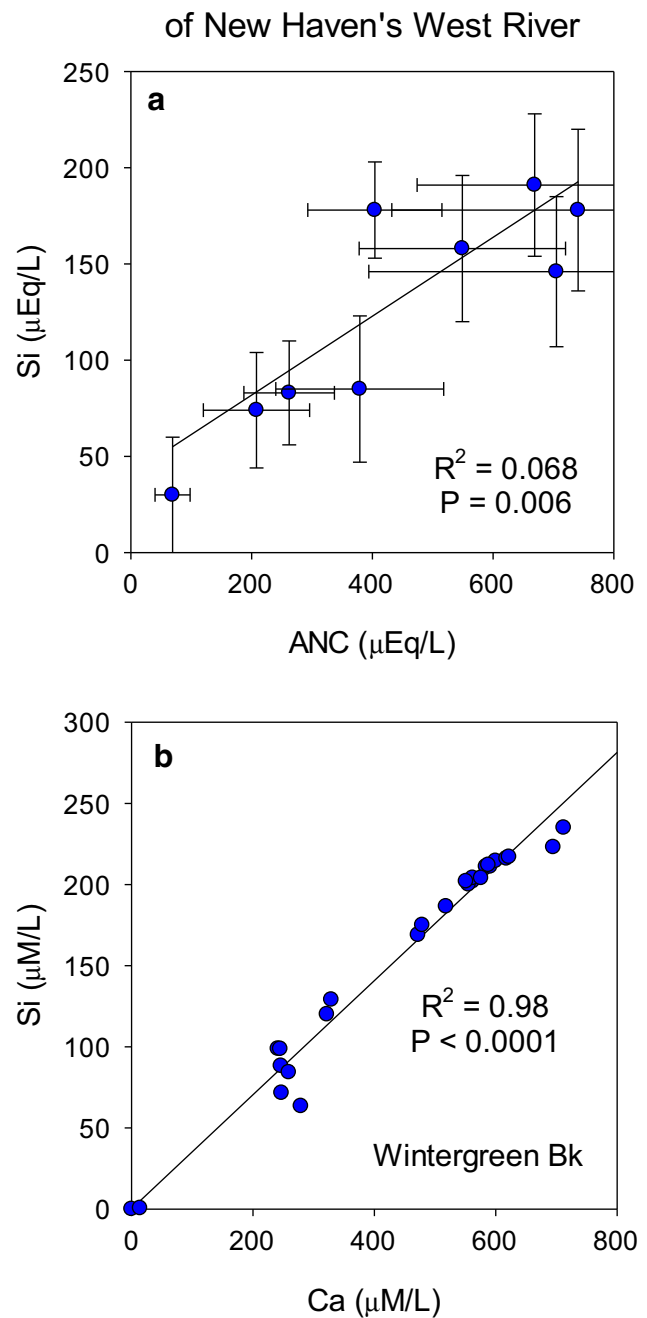
Cr levels were slightly less stable than ANC over the period of carbonation. Samples C1, C2, C3, and C4 had relative standard deviations of 10.1, 15.6, 6.0, and 10.2%, respectively, for 1 through 8 weeks of carbonation treatment. These small differences are among separate physical samples, not the same samples measured at different points in time. Thus, the changing values include differences due to sample heterogeneity as well as experimental variations from week to week.

The quick change in weathering rates after a week of carbonation treatment was as unexpected for Cr(VI) as for ANC, although Cr(VI) weathering from cement cured for 28 days was observed to increase after 8 weeks of carbonation in an enriched CO₂ atmosphere. The increase after exposure to carbon dioxide is troubling, as it indicates that leaching of toxic Cr(VI) from installed concrete materials is likely to increase over time.

Table 3 Silica weathering rates for each experiment derived from slopes of Si concentration vs. time. Concentrations have been multiplied by 70 to reflect the volume:surface ratio used in our experiment

Weeks of carbonation	Sample	Si weathering rate (mEq/L m ² h)	R ²
0	C1	1.47	1.00
1	C1	0.61	0.99
2	C1	0.63	1.00
3	C1	0.61	1.00
8	C1	0.94	0.99
0	C2	2.16	0.98
1	C2	0.52	0.98
2	C2	0.48	0.89
3	C2	0.38	0.89
8	C2	0.96	1.00
0	C3	1.31	1.00
1	C3	0.98	1.00
2	C3	0.91	1.00
3	C3	0.90	1.00
8	C3	1.24	0.99
0	C4	1.85	0.96
1	C4	1.12	0.92
2	C4	1.13	0.94
3	C4	1.05	0.96
8	C4	1.14	0.99

Fig. 6 **a** Dissolved substances in tributaries of New Haven's West River for baseflow conditions, and **b** the same for a major storm. For **a**, each point represents the average of 12 monthly baseflow measurements for one tributary. Error bars indicate one standard deviation around the means and reflect sample heterogeneity. Data in **b** are for one storm on Wintergreen Brook



3.3 Silica

Though present at low levels, silica was well above detection limits and notable in increasing continuously over the course of our recirculation experiments and showing no sign of stabilizing even after 2.5 h (Fig. 4). In separate experiments, we found that Si levels continued to increase for as long as 3 days of recirculation (data not shown).

Slopes of the linear equations fitted to the silica data across experiments (Table 3) were normally distributed around a mean of 1.02 mEq/L m² h, with a standard deviation of 0.45 mEq/L m² h, a range of 0.38 to 2.16 mEq/L m² h, and outliers at 2.2 and 1.9 mEq/L m² h (corrected for area). The dissimilar behavior of Si compared to cations and anions (Si is almost completely un-ionized at our experimental pH) suggests it may come from different reactions or even

different minerals comprising the aggregate. The reactions might include hydration and rearrangement of one of the amorphous aluminosilicate minerals in the cement matrix. For example, reaction of C-S-H gel with Al and sulfate or chloride to form Friedel's salt or Ettringite could release Si. Alternatively, exposed feldspars or other aluminosilicates in the concrete's aggregate might weather to release Si.

It appears that silica weathers at a constant rate from each concrete material. The low Si levels and continuing release may indicate that Si weathering has not reached equilibrium. To the extent that Si release is time invariant over periods similar to contact of runoff with concrete, it seems that silica might be used as an indicator of stormwater contact with concrete surfaces. Clearly, such a use would need to take into account other Si derived from abundant aluminosilicate rocks.

It is interesting and surprising that concrete, generally thought of as mainly calcareous, might be providing significant amounts of Si as well as Ca. In separate research, we measured a broad suite of substances in tributaries of New Haven's West River. In these watersheds, land use varied from completely undeveloped to fully urbanized. Results showed that both ANC (dominated by Ca) and Si levels increased with the extent of land development and presumably the amount of concrete surfaces (Fig. 6). The two data points in the lower left hand corner of Fig. 6b represent locations with little or no development or concrete surfaces, and they may reflect the local natural background. Points farther to the right may exhibit Si and Ca added through weathering of concrete. The typical levels of Si observed in Fig. 6 could be produced in several hours of weathering under conditions like those in our experiments.

4 Conclusions

When testing the leachability of concrete in lab studies, it is generally necessary to grind samples to increase surface area and reduce water contact times. This practice leads to exposure of fresh surfaces that may not behave like weathered concrete does in the field. Our tests indicate that exposure of concrete to a 5% CO₂ atmosphere for as little as 1 week produces a stable material that can be used to study the behavior of concrete similar to that which has been in place for several years. This is the main conclusion of the current research.

Following carbonation, leaching of ANC occurs at a reduced rate and approaches steady state within a few

hours. By contrast, Cr leaching not only increases after carbonation to simulate aging (compared to pre-carbonation rates) but also stabilizes within a few hours of contact with water. Calcium and bicarbonate are the main cation and anion released by the carbonated concrete, but sulfate is unexpectedly high. Silica differs from all the other substances we studied by increasing for several hours or even days of contact between water and concrete. Our results support the idea that concrete in the built environment may be an important contributor of ANC to rivers and streams (Connor et al. 2014), rivalling limestone when taking into account area and contact time. These measurements also raise the possibility that concrete weathering may be a significant contributor of Si, comparable to aluminosilicate rocks for common field conditions in urban areas.

References

- Arakaki, T., & Mucci, A. (1995). A continuous and mechanistic representation of calcite reaction-controlled kinetics in dilute solutions at 25 degrees C and 1 atm total pressure. *Aquatic Geochemistry*, *1*, 105–130.
- Baker, A., Cumberland, S., & Hudson, N. (2008). Dissolved and total organic and inorganic carbon in some British rivers. *Area*, *40*, 117–127.
- Bodaghpour, S., Joob, N. B., & Ahmadib, S. (2012). A review on the existence of chrome in cement and environmental remedies to control its effects. *International Journal of Geology*, *6*, 62–67.
- Brogren, C., & Karlsson, H. T. (1997). A model for prediction of limestone dissolution in wet flue gas desulfurization applications. *Industrial & Engineering Chemistry Research*, *36*, 3889–3897.
- Busenberg, E., & Plummer, L. N. (1982). The kinetics of dissolution of dolomite in CO₂-H₂O systems at 1.5 to 65 degrees C and 0 to 1 atm pCO₂. *American Journal of Science*, *282*, 45–78.
- Chen, Q. Y., Tyrer, M., Hills, C. D., Yang, X. M., & Carey, P. (2009). Immobilisation of heavy metal in cement-based solidification/stabilisation: a review. *Waste Management*, *29*, 390–403.
- Connor, N. P., Sarraino, S., Frantz, D. E., Bushaw-Newton, K., & MacAvoy, S. E. (2014). Geochemical characteristics of an urban river: influences of an anthropogenic landscape. *Applied Geochemistry*, *47*, 209–216.
- Dayal, R., & Reardon, E. J. (1994). Carbon-14 behaviour in a cement-dominated environment: implications for spent CANDU resin waste disposal. *Waste Management*, *14*, 457–466.
- Dreybrodt, W., Lauckner, J., Zaihua, L., & Svensson, B. (1996). The kinetics of the reaction CO₂ + H₂O → HCO₃⁻ as one of the rate-limiting steps for the dissolution of calcite in the system H₂O-CO₂-CaCO₃. *Geochimica et Cosmochimica Acta*, *60*, 3375–3381.
- Duguid, A., & Scherer, G. W. (2010). Degradation of oilwell cement due to exposure to carbonated brine. *International Journal of Greenhouse Gas Control*, *4*, 546–560.

- Eisenlohr, L., Meteva, K., Gabrovšek, F., & Dreybrodt, W. (1999). The inhibiting action of intrinsic impurities in natural calcium carbonate minerals to their dissolution kinetics in aqueous H₂O–CO₂ solutions. *Geochimica et Cosmochimica Acta*, *63*, 989–1001.
- Engelsen, C. J., van der Sloot, H. A., Wibetoe, G., Petkovic, G., Stoltenberg-Hansson, E., & Lund, W. (2009). Release of major elements from recycled concrete aggregates and geochemical modelling. *Cement and Concrete Research*, *39*, 446–459.
- Espinosa, D. C. R., & Tenório, J. A. S. (2000). Laboratory study of galvanic sludge's influence on the clinkerization process. *Resources, Conservation and Recycling*, *31*, 71–82.
- Groves, G., Rodway, D., & Richardson, I. G. (1990). The carbonation of hardened cement pastes. *Advances in Cement Research*, *3*, 117–125.
- Herlihy, A. T., Stoddard, J. L., & Johnson, C. B. (1998). The relationship between stream chemistry and watershed land cover data in the mid-Atlantic region, US. *Water Air and Soil Pollution*, *105*, 377–386.
- Hills, L. M., & Johansen, V. C. (2007). *Hexavalent chromium in cement manufacturing: literature review*. Skokie: Portland Cement Association.
- Hyvert, N., Sellier, A., Duprat, F., Rougeau, P., & Francisco, P. (2010). Dependency of C-S-H carbonation rate on CO₂ pressure to explain transition from accelerated tests to natural carbonation. *Cement and Concrete Research*, *40*, 1582–1589.
- John, D. A. S., Poole, A. B., & Sims, I. (1998). *Concrete petrography: a handbook of investigative techniques*. London: Arnold.
- Kayhanian, M., Vichare, A., Green, P. G., & Harvey, J. (2009). Leachability of dissolved chromium in asphalt and concrete surfacing materials. *Journal of Environmental Management*, *90*, 3574–3580.
- Lancia, A., Musmarra, D., & Pepe, F. (1997). Mass transfer between a fixed bed of limestone particles and acid solutions. *Industrial & Engineering Chemistry Research*, *36*, 3859–3865.
- Leisinger, S. M., Bhatnagar, A., Lothenbach, B., & Johnson, C. A. (2014). Solubility of chromate in a hydrated OPC. *Applied Geochemistry*, *48*, 132–140.
- Luquot, L., Abdoulghafour, H., & Gouze, P. (2013). Hydrodynamically controlled alteration of fractured Portland cements flowed by CO₂-rich brine. *International Journal of Greenhouse Gas Control*, *16*, 167–179.
- McNeill, L. S., McLean, J. E., Parks, J. L., & Edwards, M. (2012). Hexavalent chromium review, part 2: chemistry, occurrence, and treatment. *Journal American Water Works Association*, *104*, 39–40.
- Müllauer, W., Beddoe, R. E., & Heinz, D. (2012). Effect of carbonation, chloride and external sulphates on the leaching behaviour of major and trace elements from concrete. *Cement and Concrete Composites*, *34*, 618–626.
- National Atmospheric Deposition Program (2010). *NADP map viewer*. Campaign: NADP Program Office, Illinois State Water Survey.
- Neves, R., Branco, F., & De Brito, J. (2013). Field assessment of the relationship between natural and accelerated concrete carbonation resistance. *Cement and Concrete Composites*, *41*, 9–15.
- Noiriel, C., Luquot, L., Madé, B., Raimbault, L., Gouze, P., & Van Der Lee, J. (2009). Changes in reactive surface area during limestone dissolution: an experimental and modelling study. *Chemical Geology*, *265*, 160–170.
- Pepe, F. (2001). Dissolution of finely ground limestone particles in acidic solutions. *Industrial & Engineering Chemistry Research*, *40*, 5378–5385.
- Plummer, L. N., & Wigley, T. M. L. (1976). The dissolution of calcite in CO₂-saturated solutions at 25° C and 1 atmosphere total pressure. *Geochimica et Cosmochimica Acta*, *40*, 191–202.
- Plummer, L. N., Wigley, T. M. L., & Parkhurst, D. L. (1978). The kinetics of calcite dissolution in CO₂-water systems at 5 degrees to 60 degrees C and 0.0 to 1.0 atm CO₂. *American Journal of Science*, *278*, 179–216.
- Pu, Q., Jiang, L. H., Xu, J. X., Chu, H. Q., Xu, Y., & Zhang, Y. (2012). Evolution of pH and chemical composition of pore solution in carbonated concrete. *Construction and Building Materials*, *28*, 519–524.
- Rauch, H. W., & White, W. B. (1977). Dissolution kinetics of carbonate rocks: 1. Effects of lithology on dissolution rate. *Water Resources Research*, *13*, 381–394.
- Reardon, E. J., & Fagan, R. (2000). The calcite/portlandite phase boundary: enhanced calcite solubility at high pH. *Applied Geochemistry*, *15*, 327–335.
- Schiopu, N., Tiruta-Barna, L., Jayr, E., Mehu, J., & Moszkowicz, P. (2009). Modelling and simulation of concrete leaching under outdoor exposure conditions. *Science of the Total Environment*, *407*, 1613–1630.
- Sinyoung, S., Asavapisit, S., Kajitvichyanukul, P., & Songsiririthigul, P. (2011a). Speciation of Cr in cement clinkers obtained from co-burning with Cr₂O₃. *Nuclear Instruments & Methods in Physics Research Section a-Accelerators Spectrometers Detectors and Associated Equipment*, *649*, 210–212.
- Sinyoung, S., Songsiririthigul, P., Asavapisit, S., & Kajitvichyanukul, P. (2011b). Chromium behavior during cement-production processes: a clinkerization, hydration, and leaching study. *Journal of Hazardous Materials*, *191*, 296–305.
- Suarez, D. L. (1983). Calcite supersaturation and precipitation kinetics in the Lower Colorado River, All-American Canal and East Highline Canal. *Water Resources Research*, *19*, 653–661.
- Ukawa, N., Takashina, T., Oshima, M., & Oishi, T. (1993). Effects of salts on limestone dissolution rate in wet limestone flue gas desulfurization. *Environmental Progress*, *12*, 294–299.
- Van Gerven, T., Cornelis, G., Vandoren, E., Vandecasteele, C., Garrabrants, A. C., Sanchez, F., & Kosson, D. S. (2006). Effects of progressive carbonation on heavy metal leaching from cement-bound waste. *AIChE Journal*, *52*, 826–837.
- Wang JG (1994) Sulfate attack on hardened cement paste. *Cement and Concrete Research* *24*, 735–742.
- Wang, S., & Vipulanadan, C. (2000). Solidification/stabilization of Cr(VI) with cement - leachability and XRD analyses. *Cement and Concrete Research*, *30*, 385–389.
- Williams, M., Hopkinson, C., Rastetter, E., Vallino, J., & Claessens, L. (2005). Relationships of land use and stream solute concentrations in the Ipswich River basin, northeastern Massachusetts. *Water Air and Soil Pollution*, *161*, 55–74.