Density Driven Damage Mechanics (D3-M) Model for Concrete II: Fully Coupled Chemo-Mechanical Damage

Pavitra T. Murru[a], Zachary Grasley[a], Christa Torrence[b], K.R. Rajagopal[c] and Edward Garboczi[d]

[a]Zachry Department of Civil Engineering, 3136 TAMU, College Station, TX 77843-3136, United States; [b]Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843-3136, United States; [c]J. Mike Walker '66 Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843-3136, United States; [d]National Institute of Standards and Technology, Boulder, Colorado, United States

ARTICLE HISTORY
Compiled May 20, 2020

ABSTRACT
In Part I, a density driven damage mechanics (D3-M) approach and its application to model mechanical damage in concrete are presented. In this study, chemical and chemo-mechanical damage in concrete are modeled using the D3-M approach. It is proposed that reductions in local density in certain regions, created when concrete is subjected to chemical attack or a coupled chemical-mechanical loading, result in reduced stiffness and strength of the material. The D3-M modeling approach stands out among the past efforts to predict the response of concrete to mechanical and chemical stimuli due to its ability to effectively model the mechanical, chemical, and coupled mechanical-chemical responses of concrete using a consistent framework and a single constitutive equation for both types of damage. Model simulations indicate that the response of the material to a scenario where chemical and mechanical loads are acting simultaneously cannot be considered equivalent to the response obtained by superposing the separate responses to independent mechanical and chemical loads.

KEYWORDS
Leaching; Coupled load; Density; Continuum damage mechanics; Finite element modeling

1. Introduction

1.1. *Background*

Damage in concrete is primarily due to mechanical loads, chemical attack, or a combination of these. Although there has been a significant amount of work carried out on simulating the effects of mechanical loading on the structural functionality of concrete quantified through parameters such as the strength and the stiffness, simulations of the chemical degradation of these parameters are much less common. There are primarily two reasons for this: i) chemical degradation almost always occurs simultaneously with mechanical deterioration of a material (in any structure) making it a complex task to

CONTACT Pavitra T. Murru. Email: pavitratejaswi@tamu.edu

understand and model the effects of chemical attack separately on the material, and ii) degradation of strength and stiffness is typically modeled as a function of some measure of stress or strain magnitude, which may not prove useful in capturing chemical degradation since a degrading body may be stress and strain free.

In the context of concrete (or, more generally, cementitious materials), chemical attack generally refers to leaching of calcium hydroxide (CH), sulfate attack, alkali-silica reaction (ASR), carbonation, and chloride attack. This study is confined to modeling the effects of leaching of CH in combination with mechanical degradation for ordinary Portland cement concrete. Researchers have proposed different ways to model chemical phenomena separately and/or coupled with mechanical loads in concrete. Le Bellego et al. (Le Bellégo *et al.* 2003) considered the method previously used by Gerard (Gérard 1996) and Kuhl et al. (Kuhl *et al.* 2000) to model chemical damage by adding a chemical damage parameter to the mechanical damage parameter in the stress-strain relation of the scalar (mechanical) damage model proposed by Mazars (Mazars 1984). According to this method, damage due to chemical leaching and mechanical degradation takes place entirely independent of each other such that the chemical damage parameter is solely a function of the concentration of calcium ions in the solution and the mechanical damage parameter depends on the mechanical strains. Carde and François proposed a model to incorporate the damage caused by chemical leaching by using a damage function to describe mechanical effects and an aging function to account for chemical effects on the reduction of the elastic modulus of cement paste. While the damage function is dependent on strain, the aging function depends on calcium content in the solid phase, which in turn is defined to be a function of the depth of the degraded (leached) zone (Carde and François 1997a). While Ulm et al. (Ulm *et al.* 1999) modeled chemo-mechanical coupling related to leaching based on the framework proposed by Coussy (Coussy 1995), where the chemical damage is considered by introducing a dependence of the elastic modulus on the volume fraction of the portlandite (CH), Bangert et al. (Bangert *et al.* 2003) modeled damage due to leaching as a scalar dependent on the local porosity in the material. Both of these preceding approaches are similar in concept to the approach proposed here since the volume fraction of a given phase is an intensive, measurable parameter that is related to local density. However, Bangert et al. (Bangert *et al.* 2003) and Ulm et al. (Ulm *et al.* 1999) have not generalized this approach such that it can be applied to simultaneous chemical and mechanical degradation in a unified, consistent manner using local density as an internal variable.

1.2. *Research Objective*

The objective of the current study is to unify the modeling of damage associated with chemical effects and damage associated with mechanical loads using the density driven damage mechanics (D3-M) model (Murru *et al.* Under review), which is briefly reviewed in the next section. This includes specific tasks of modeling the mechanical damage of chemically leached concrete and modeling the damage in concrete subjected to mechanical loading while being exposed to chemical leaching. It will thereby be established that the D3-M approach is able to demonstrate the effect of simultaneous chemical leaching and mechanical loading on the stiffness and the strength of the material.

1.3. *Micro-mechanisms Linking Density to Damage*

Concrete is an inhomogeneous material that contains various flaws such as pores (gel and capillary), micro-cracks and the interfacial transition zone (ITZ) regions even before it is exposed to any kind of conventional loading. The ITZ regions are characterized by high porosity and the reduction of cement near the surface of embedments (aggregates, fibers, steel reinforcement) caused by the inability of the cement particles to pack efficiently around these embedments ("wall effect") (Scrivener *et al.* 2004). Within the ITZ, there is a gradation of porosity, which is relatively high at the innermost portion of this region and decreases to the value of the bulk cement paste as one moves away from the aggregate surface into the bulk cement paste. The extra pore space in concrete, originally a result of the wall effect, is mostly filled up by deposits of CH and by deposits of calcium silica hydrate (C-S-H) leaving only a little extra average pore content within the ITZ (Diamond and Huang 2001). Leaching of CH leads to a complete removal of the portlandite and a progressive decalcification of the C-S-H (Jebli *et al.* 2018). This results in replacement of the spaces filled with these materials with pores, thus leading to increased porosity and hence reduced local density. Based on the D3-M theory, these low density regions are the source for the initiation of damage and the intensity of damage in concrete increases as these low-density regions propagate with progress in loading (mechanical as well as chemical). Additionally, CH is a part of the composition of both the ITZ and mortar (a mixture of cement paste and fine aggregate (sand)) in concrete. In the current study, the term "leaching" in the context of mortar is supposed to refer to the leaching of CH from cement paste. Although it is inferred by Jebli et.al. (Jebli *et al.* 2018) that there is a significant leaching of the portlandite from the ITZ during this chemical attack based on the study carried out by Carde and François (Carde and François 1997b), it is difficult to understand in what proportions CH is being leached out of the ITZ versus the bulk cement paste. Hence, the possibility of CH being leached out of either or both of the ITZ and bulk cement paste is explored as part of this research.

2. Theoretical Framework

This section introduces the theoretical formulation used to model the mechanical response of chemically leached concrete and the coupled mechanical-chemical response of concrete by first giving a brief account of the D3-M model used in the context of a pure mechanical loading scenario discussed in Part I (Murru *et al.* Under review). This is followed by outlining the procedure to introduce the chemical damage component into the D3-M approach. A description of the microstructure used for modeling is also presented.

2.1. *Review of D3-M Theory*

A constitutive model of the form

$$\mathbf{B} = \alpha_1 \mathbf{I} + \alpha_2 \mathbf{T} + \alpha_3 \mathbf{T}^2, \quad (1)$$

where α_1, α_2, α_3 depend on ρ, $tr(\mathbf{T})$, $tr(\mathbf{T}^2)$ and $tr(\mathbf{T}^3)$ (tr is the trace operator), $\mathbf{B}$ is the right Cauchy Green tensor, $\mathbf{T}$ is the Cauchy stress tensor and ρ is the current density of the material, when linearized according to the assumption that the displacement gradient is small will lead to

$$\boldsymbol{\epsilon} = \beta_1 \mathbf{I} + \beta_2 \mathbf{T} + \beta_3 \mathbf{T}^2, \tag{2}$$

where $\boldsymbol{\epsilon}$ is the infinitesimal strain measure. Here, β_1, β_2, β_3 depend on ρ, $tr(\mathbf{T})$, $tr(\mathbf{T}^2)$ and $tr(\mathbf{T}^3)$ (Rajagopal 2007). When displacement gradients are small, the law of conservation of mass can be represented as

$$\rho = \frac{\rho_R}{det(\mathbf{F})} \approx \frac{\rho_R}{1 + tr(\boldsymbol{\epsilon})} \approx \rho_R[1 - tr(\boldsymbol{\epsilon})], \tag{3}$$

where ρ_R is the reference density of the material, $\mathbf{F}$ is the deformation gradient and det is the determinant operator.

In the D3-M approach, it is proposed that damage can be defined on the basis of changes in local density of the material, and the damage is manifested via reductions in the stiffness of the material. Therefore, it is assumed that the evolution of the material stiffness can be represented as

$$E = E_R[1 + \gamma(\rho - \rho_R)]. \tag{4}$$

Here, E and E_R are the current and reference values of the Young's modulus and γ is a phenomenological coefficient. γ is supposed to indicate the extent of dependence of the drop in stiffness on the changes in density of the material. Based on this definition of evolution of material stiffness and the law of conservation of mass defined in Eq.(3), an implicit constitutive relation for the current study is then derived from Eq.(2) such that $\beta_1 = -\frac{\nu}{E_R[1-\gamma\rho_R tr(\boldsymbol{\epsilon})]} tr(\mathbf{T})$, $\beta_2 = \frac{1+\nu}{E_R[1-\gamma\rho_R tr(\boldsymbol{\epsilon})]}$ and $\beta_3 = 0$ to obtain

$$\boldsymbol{\epsilon} = -\frac{\nu}{E_R[1 - \gamma\rho_R tr(\boldsymbol{\epsilon})]} tr(\mathbf{T})\mathbf{I} + (\frac{1 + \nu}{E_R[1 - \gamma\rho_R tr(\boldsymbol{\epsilon})]})\mathbf{T}. \tag{5}$$

Here, ν is the Poisson's ratio of the material. It is certainly possible that Poisson's ratio, similar to Young's modulus, is also a density-dependent parameter. In the current study, only Young's modulus is defined as a function of density for the sake of computational simplicity. The above defined constitutive relation is able to account for damage in concrete based on local density changes due only to mechanical loading. The constitutive model to account for chemical damage and a combination of chemical and mechanical damage is formulated next.

2.2. *Incorporation of Damage due to Chemical Leaching into D3-M Model*

Conservation of mass may be expressed as

$$\frac{d\rho}{dt} = -\rho div[\mathbf{v}], \tag{6}$$

where ρ is the mass density, $\frac{d}{dt}$ is a material time derivative, $\mathbf{v}$ is the material velocity, and div is the divergence operation. Though all the equations in the current study are defined at some spatial point defined by position vector $\mathbf{x}$ and at time t, the variables are not represented explicitly as functions of $\mathbf{x}$ and t in order to have simpler expressions. From Eq.(6), it is clear that the only means by which a continuous chunk of material may experience density changes is from changes in volume; by definition, in mechanics of a continuous material the material time derivative considers a fixed chunk of continuous media and mass losses are not allowed. Thus, it is clear that mechanics of a single continuum does not provide a suitable framework for considering environmentally induced degradation that involves density changes driven by mass loss rather than strictly volume change. Mixture theory is an extension of continuum mechanics whereby one considers that, at any moment in time t, we have a mixture of N distinct species, each of which is a continuum (Grasley and Rajagopal 2012)(Prasad and Rajagopal 2006)(Tao *et al.* 2001). Furthermore, the mixture of these N species likewise is a continuum, and the mixture occupies the same space as that of the N species at any moment in time. At any point in the body at any moment in time, one might track the motion of any individual species with respect to itself, another species, or the mixture. Utilizing conservation of mass for a mixture (Eq.(6)), one can solve for the local density field of the load-bearing (typically solid) phases within a mixture as

$$\frac{d\rho^i}{dt} = \dot{\rho}^i_{gen} - \rho^i div[\mathbf{v}^i], \tag{7}$$

where ρ^i is the partial density of the solid, load-bearing phase (species i) of interest, which varies as a function of spatial location ((x)) and time (t) (argument suppressed in the equations for clarity), $\frac{d}{dt}$ is the material time derivative, $\dot{\rho}^i_{gen}$ is the volume-specific rate of mass production of species and $\mathbf{v}^i$ is the velocity of species i. In a porous geomaterial, solid phases/species may be presumed to have minimal diffusion in comparison to dissolved species (i.e., solid phases first undergo dissolution, then the dissolved species diffuse rather than solids diffusing themselves) such that $\mathbf{v}^i = \mathbf{v}$, which is the velocity of the mixture. Furthermore, from the conservation of mass of the mixture, one finds that $div[\mathbf{v}] = \frac{1}{J}\frac{dJ}{dt}$, where J is the determinant of the deformation gradient. Thus, we may rewrite Eq.(7) as

$$\frac{1}{\rho^i}\frac{d\rho^i}{dt} = \frac{1}{\rho^i}\dot{\rho}^i_{gen} - \frac{1}{J}\frac{dJ}{dt}. \tag{8}$$

The first term on the right hand side of Eq.(8) is a constitutive relation for the normalized mass production rate associated with chemical reactions and phase transitions (e.g, dissolution); this rate can be written in terms of the normalized production or consumption of other species or phases or, more generally, expressed as a phenomenological function of time ($g(\mathbf{x}, t)$) based on experimental measures. For the ease of mathematical computation, we further assume that there exists a smooth function $f(\mathbf{x}, t)$ such that

$$g(\mathbf{x}, t) = \frac{df(\mathbf{x}, t)}{dt}. \tag{9}$$

Then, we can write

$$\frac{1}{\rho^i}\frac{d\rho^i}{dt} = \frac{df(\mathbf{x}, t)}{dt} - \frac{1}{J}\frac{dJ}{dt}, \tag{10}$$

which, after integration, results in

$$\rho^i(\mathbf{x},t) = \frac{{\rho_R}^i(\mathbf{x},t)e^{f(\mathbf{x},t)}}{J(\mathbf{x},t)}. \tag{11}$$

Eq.(11) demonstrates how local density evolves as a function of dissolution (captured by f) and by mechanical deformations (captured by J). For a material experiencing dissolution of the solid phase, the normalized mass production may be expressed in terms of the log of the growth of porosity ($\Delta p(t)$) such that

$$f(t) = \ln(1 - \Delta p(t)), \tag{12}$$

and the rate is thus

$$\frac{df(t)}{dt} = -\frac{d(\Delta p(t))}{dt}\frac{1}{1 - \Delta p(t)}. \tag{13}$$

Substituting Eqs.(12) into (11) results in

$$\rho^i(\mathbf{x},t) = \frac{{\rho^i}_R(\mathbf{x},t)(1 - \Delta p(t))}{J(\mathbf{x},t)}. \tag{14}$$

Eq.(14) describes the current, partial density of species i (ρ^i) in terms of the volume specific mass change due to production or consumption of that species, the reference configuration partial mass density of the species (${\rho^i}_R$), and the volumetric deformation of the mixture to which that species belongs. Thus, the first term allows one to account for changes in local density associated with chemical effects while the second term allows one to account for changes in local density associated with mechanical effects. Notice that if the mixture is comprised solely of species i and there are no mass changes due to chemical effects (and thus no porosity changes), then we have

$$\rho^i = \frac{{\rho^i}_R}{J} \approx \frac{{\rho^i}_R}{1 + tr[\boldsymbol{\epsilon}]} \approx {\rho^i}_R(1 - tr[\boldsymbol{\epsilon}]). \tag{15}$$

When the displacement gradients are small, as is usually the case with deformations in concrete, Eq.(14) can be written as

$$\rho^i = \frac{{\rho^i}_R(1 - \Delta p^i)}{(1 + tr[\boldsymbol{\epsilon}])} \approx {\rho^i}_R(1 - \Delta p^i)(1 - tr[\boldsymbol{\epsilon}]), \tag{16}$$

where Δp^i is the growth of porosity in species i. The final constitutive equation is derived by substituting Eq.(16) for ρ_i in the original constitutive equation, such that $\beta_1 = -\frac{\nu^i}{E_R^i[1+\gamma(\rho^i-\rho_R^i)]}tr(\mathbf{T})$, $\beta_2 = \frac{1+\nu^i}{E_R^i[1+\gamma(\rho^i-\rho_R^i)]}$ and $\beta_3 = 0$ to find

$$\boldsymbol{\epsilon} = -\frac{\nu^i}{E_R^i[1 + \gamma(\rho^i - \rho_R^i)]}tr(\mathbf{T})\mathbf{I} + (\frac{1 + \nu^i}{E_R^i[1 + \gamma(\rho^i - \rho_R^i)]})\mathbf{T}. \tag{17}$$

Here, E_R^i is the initial Young's modulus and ν^i is the Poisson's ratio of the species i of the microstructure. It is important to note that the species i in this study refers to the part of the mixture that contributes to the density and stiffness of the mixture. That is, if we consider the mixture to be a combination of solid and dissolved species, the species with the subscript i refers to the solid species part, which contributes to the mixture's load-bearing capacity via the property of elastic stiffness. On the other hand, the mixture itself refers to one of the three components of concrete: aggregate, mortar or the ITZ. In case of mortar or the ITZ, CH is one of the components of its solid species and its leaching is likely to cause additional porosity and thus reduce the stiffness of the mixture itself (either mortar or the ITZ).

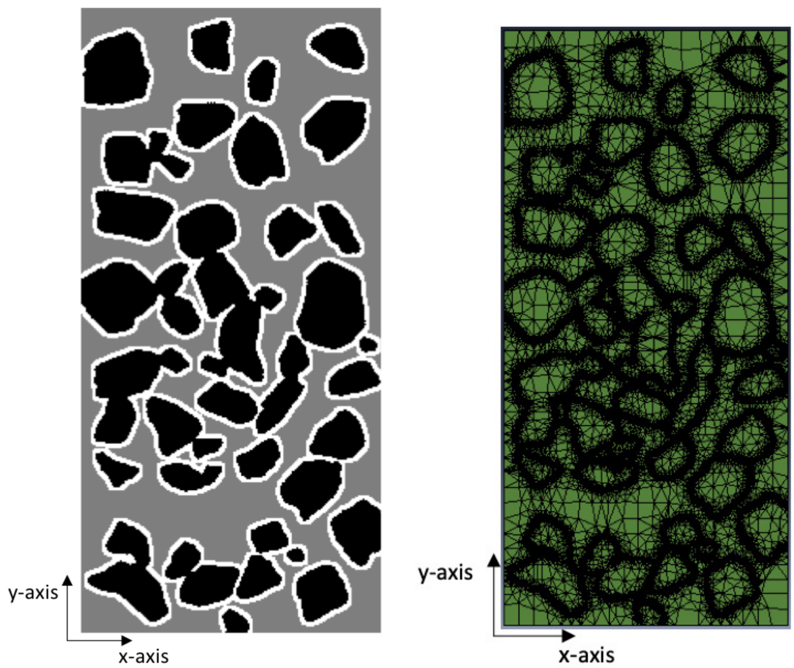
2.3. *Microstructure Generation*

A planar microstructure, 186 mm by 387 mm, consisting of three components- coarse aggregates (40 % of the total microstructure area) embedded in the mortar, with a thin layer of the ITZ around coarse aggregates as shown in Figure 1(a), is used for modeling in the current study. The microstructure is such that the coarse aggregates are randomly positioned within the mortar matrix and have the ITZ layers around them. To begin with, a microstructure with only the coarse aggregates and the mortar is created by using a MATLAB program, developed based on the Anm model introduced by Qian et al. (MatLab 2012)(Qian *et al.* 2016). The mathematical data related to the shape of real 3-dimensional aggregates captured by spherical harmonic expansions based on X-ray computed tomographic images are projected onto a third plane from which 2-dimensional shapes are created. These 2-dimensional shapes are grouped, based on a size measure representative of the sieve sizes used for aggregates in concrete ranging from 7.5 mm to 66 mm, and then packed randomly into an empty domain to a fixed area percentage (as per our requirement) of coarse aggregates. In addition, the coarse aggregates are allowed to cut across the boundaries but the portion extending beyond the domain is not considered part of the microstructure, simulating a concrete core specimen. The resulting image is binarized and the aggregate edges are detected and further dilated to a thickness of approximately 1.6 mm to become the ITZ such that the ITZ accounts for 10 % of the total microstructure area. The ITZ thickness considered is beyond the experimentally observed range of 20 μm - 40 μm (Young *et al.* 2002) so as to limit the number of extremely small-sized elements within and around the ITZ. A more detailed discussion on the implications for the coarse approximation can be found in Part I (Murru *et al.* Under review). The creation of the ITZ is followed by creating a finite element mesh in OOF2 and importing it to ABAQUS to run the final simulations (Langer *et al.* 2017)(Langer *et al.* 2008)(Abaqus Users Manual 2013).

The simulations are further carried out in ABAQUS as plane stress problems using the constitutive equation shown in Eq.(17), which is formulated as a VUMAT subroutine of ABAQUS Explicit Analysis.

3. Modeling and Results

Leaching of CH refers to dissolution of solid CH by a liquid passing through concrete. With a reduction in the volume of CH in concrete, the local porosity goes up. This leads to a drop in the density of the material. CH is a part of both the ITZ and mortar phases (the term "phase" is identical to the term "species" used in the previous sections, which is an abuse of terminology as the species under consideration are not two phases of a particular material but we shall yet use such terminology as it



(a) Test microstructure

(b) Finite element mesh for the test microstructure

Figure 1. Test microstructure (186 mm by 387 mm) representing a section of a cored cylinder using realistic aggregate shapes surrounded by an interfacial transition zone. Finite element mesh created by choosing the element type to be a mix of quadrilateral (CPS4R in ABAQUS) and triangular (CPS3 in ABAQUS), with homogeneity index of 0.99 and without horizontal or vertical periodicity.

is commonly used in the literature.) of concrete. Hence, it is possible that there is density reduction in either or both of these phases when leaching happens. Two types of scenarios are simulated in this study: i) mechanical response of already-leached concrete to uni-axial compression, and ii) chemo-mechanical response of concrete that is subjected to uni-axial compression while being leached, which are illustrated in Figure 2. In Figure 2, the clockwise path starting from κ_R leading to κ_1 via $\kappa_{R-Leached}$ is the first scenario and the anticlockwise path leading to κ_2 starting from κ_R is the second scenario. Here a configuration of a body refers to the set of positions of the particles of that body at a given time (Spencer 2004) and κ_R is the reference configuration (stress-free configuration), $\kappa_{R-Leached}$, κ_1, and κ_2 are configurations at different points of time. While the first is essentially a superposition of the chemical and mechanical responses, the latter is a coupled response. Importantly, the same model and constitutive functions are used to model both chemical and mechanical damage. For the uni-axial compression, the microstructure is fixed at the bottom edge along the x-axis and a displacement of -0.7 mm is applied in the y-direction at the top edge as a smooth ramp loading with amplitude increasing from 0 to 1 with traction-free conditions along the lateral sides. A plane stress quasi-static analysis is carried out.

3.1. *Leached Concrete subjected to Uni-axial Compression*

The mechanical response is computed for the following cases: i) concrete that is not yet subjected to leaching, ii) concrete that has been exposed to leaching for 28 d, and

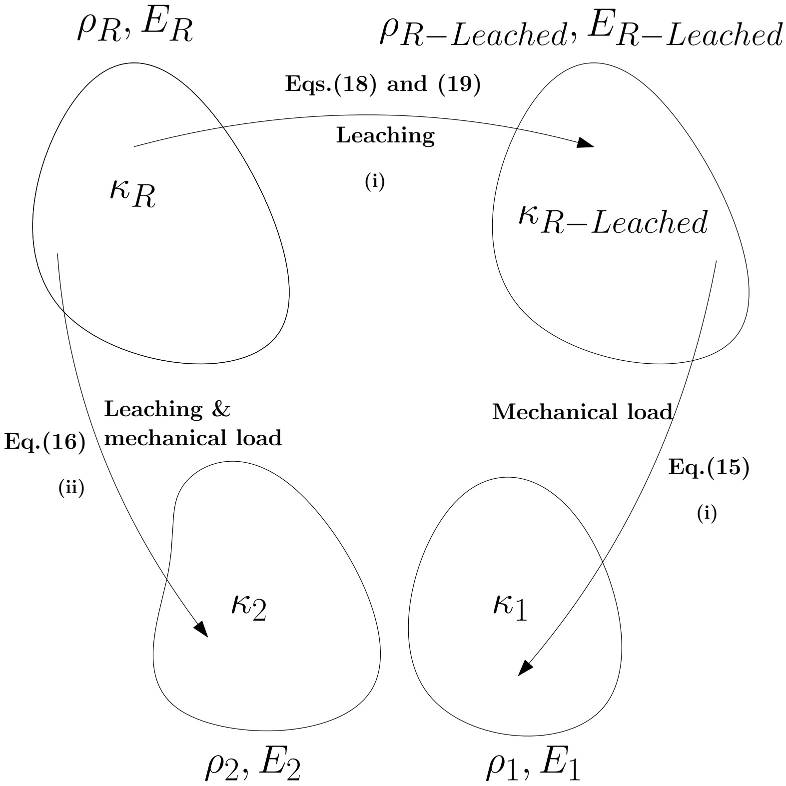


Figure 2. Reference and current configurations of concrete for two cases: (i) concrete subjected to leaching followed by mechanical loading, and (ii) concrete subjected to mechanical loading while being leached. κ_R is the reference configuration and the corresponding density and stiffness parameters are denoted as ρ_R and E_R. $\kappa_{R-Leached}$ is the configuration of concrete when it is entirely leached and the corresponding density and stiffness are represented as $\rho_{R-Leached}$ and $E_{R-Leached}$.. κ_1 is the configuration at time t for case (i) and the corresponding density and stiffness parameters are denoted as ρ_1 and E_1 respectively. κ_2 is the configuration at time t for case (ii) and the corresponding density and stiffness parameters are denoted as ρ_2 and E_2. Eqs.(18) and (19) represent the relations between densities and Young's moduli respectively at κ_R and $\kappa_{R-Leaching}$. Eq.(15) defines the relation between densities at $\kappa_{R-Leaching}$ and κ_1. Similarly, Eq.(16) represents the relation between densities at κ_R and κ_2.

iii) concrete that has been leached for 60 d. In the second and third cases, concrete is first exposed to leaching alone without any mechanical loading. In this step, the value of J would be 1 (or $tr(\epsilon) = 0$) and the density of each of the phases (i = ITZ, mortar) affected by the leaching process is computed as

$$\rho^i{}_{R-Leaching} = \rho^i{}_R \frac{m^i}{m^i{}_R} = \rho^i{}_R (1 - \Delta p^i). \tag{18}$$

This additional porosity induced by leaching will also affect the stiffness and it is assumed that the dependence of the stiffness (Young's modulus) of a component on the porosity induced by leaching is based on the relation proposed by Vichit-Vadakan et al (Vichit-Vadakan and Scherer 2002), which can be represented as

$$E^i_{R-Leached} = (1 - \Delta p^i)^3 E^i_R, \tag{19}$$

where $E^i_{R-Leached}$ is the elastic Young's modulus of component i affected by leaching and E^i_R is the reference elastic Young's modulus of the component i before being exposed to leaching. The dependence of the stiffness on porosity (or density) shown in Eq.19 is different compared to the one used in the development of the D3-M model's constitutive equation (Eq.4), in the sense that, the former has a cubic dependence and the latter a linear one. While a linear dependence had to be used in the main constitutive equation due to the choice of an infinitesimal strain based model for the D3-M approach as explained in Part I (Murru *et al.* Under review), it is possible that the relation given by Eq.19 is likely to be a better representation of the real scenario. At the three levels of leaching considered in this scenario, the total porosity values would be different. The porosity values at day 0, day 28, and day 60 are observed to be 28 %, 32 %, and 36 % respectively, as determined by Huang and Qian in their experimental study (Huang and Qian 2011). Based on these porosity values and Eqs.(18) and (19), the post-leaching reference density and stiffness (Young's modulus) values are computed for the ITZ and/or mortar phases. Then the constitutive equation defined in Eq.(17) is used to model the mechanical response of concrete prior to any leaching, where a value of 0.01 is found for γ by fitting experimental data (Huang and Qian 2011).

Three cases are considered for this simulation based on the possibility that CH could be leached from either or both of the ITZ and mortar phases. The first assumes that CH is leached from both phases proportional to their area percentage composition in the microstructure (mortar- 50 %, ITZ- 10 %). That is, in the microstructure that constitutes of 40 % coarse aggregate, 50 % mortar and 10 % ITZ, mortar and ITZ are affected by leaching while coarse aggregate remains unaffected. This implies, only 60 % of the total area is affected by leaching. Therefore, an increase in total porosity by 4 % from day 0 to day 28 would mean $\frac{1}{6}$ of this 4 % porosity increase occurs in the ITZ and $\frac{5}{6}$ of this 4 % porosity increase occurs in the mortar region. The same assumption is used for leaching at 60 d. This would lead to the reference density and Young's modulus values for the ITZ and mortar at three stages of leaching as shown in Table 1 while the properties of the coarse aggregate would remain the same. In the second case, it is assumed that CH is leached from only the mortar phase. That is, an increase in total porosity by 4 % from day 0 to day 28 would mean an increase in porosity in the mortar region by 8 % (since mortar occupies 50 % of the total area). The same assumption is used for leaching at 60 d. This would lead to the reference density and Young's modulus values for the mortar at the three stages of leaching as shown in

Table 1. Material properties at three stages of leaching when it is assumed that CH is leached out of both the ITZ and mortar

	No Leaching		28-day Leaching		60-day Leaching	
Component	Reference Density, kg/m^3	Young's Modulus (E_R), GPa	Reference Density, kg/m^3	Young's Modulus ($E_{R-Leached}$), GPa	Reference Density, kg/m^3	Young's Modulus ($E_{R-Leached}$), GPa
Mortar	2.20 x 10^3	36.0	2.05 x 10^3	29.3	1.91 x 10^3	23.4
ITZ	1.10 x 10^3	12.0	1.03 x 10^3	9.70	0.953 x 10^3	7.80
Aggregate	2.70 x 10^3	55.2	2.70 x 10^3	55.2	2.70 x 10^3	55.2

Table 2. Material properties at three stages of leaching when it is assumed that CH is leached out of only mortar phase

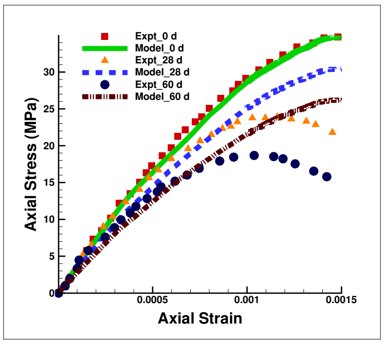
	No Leaching		28-day Leaching		60-day Leaching	
Component	Reference Density, kg/m^3	Young's Modulus (E_R), GPa	Reference Density, kg/m^3	Young's Modulus ($E_{R-Leached}$), GPa	Reference Density, kg/m^3	Young's Modulus ($E_{R-Leached}$), GPa
Mortar	2.20 x 10^3	36.0	2.02 x 10^3	28.0	1.85 x 10^3	21.3
ITZ	1.10 x 10^3	12.0	1.10 x 10^3	12.0	1.10 x 10^3	12.0
Aggregate	2.70 x 10^3	55.2	2.70 x 10^3	55.2	2.70 x 10^3	55.2

Table 2 while the properties of the ITZ and coarse aggregate would remain the same as in the reference configuration. In the third case, CH is assumed to be leached from only the ITZ. This means that an increase in total porosity by 4 % from day 0 to day 28 would be equivalent to an increase in porosity in the ITZ region by 40 %, since the ITZ regions occupy 10 % of the area. The same assumption is used for leaching at 60 d. This would lead to the reference density and Young's modulus values for the ITZ at three stages of leaching as shown in Table 3 while the properties of mortar and coarse aggregate would remain the same. Under all these scenarios, constant Poisson's ratio values of 0.25 for coarse aggregate and 0.20 for the ITZ and mortar are assumed (Murru *et al.* Under review).

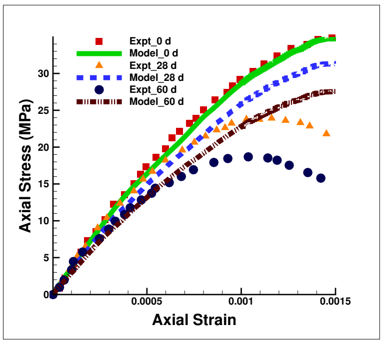
The microstructures with different sets of material properties, for the three cases as discussed above, are then subjected to uni-axial compression as described at the beginning of the current section. The model-predicted stress-strain responses are compared with the experimental observations captured by Huang and Qian as shown in Figure 3(a), Figure 3(b) and Figure 3(c) (Huang and Qian 2011). Initially, the model is fitted to the experimental data for the unleached specimen (i.e., at 0 d), such that a value of 0.01 has been assigned to the phenomenological coefficient γ of Eq.(17). Then, the model is used to predict the mechanical response of the leached concrete at 28 d and 60 d and the results are compared with the corresponding experimentally recorded response. Figure 3(c) shows that the model-prediction of the reduction in stiffness and strength due to leaching based on the assumption that CH is leached only from the ITZ is much higher than the experimentally observed reduction in strength and stiffness. *Thus, the assumption that CH is removed only from the ITZ during chemical*

Table 3. Material properties at three stages of leaching when it is assumed that CH is leached out of only ITZ phase

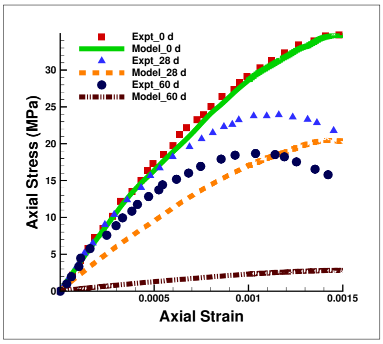
	No Leaching		28-day Leaching		60-day Leaching	
Component	Reference Density, kg/m^3	Young's Modulus (E_R), GPa	Reference Density, kg/m^3	Young's Modulus ($E_{R-Leached}$), GPa	Reference Density, kg/m^3	Young's Modulus ($E_{R-Leached}$), GPa
Mortar	2.20 x 10^3	36.0	2.20 x 10^3	36.0	2.20 x 10^3	36.0
ITZ	1.10 x 10^3	12.0	0.660 x 10^3	2.60	0.220 x 10^3	0.100
Aggregate	2.70 x 10^3	55.2	2.70 x 10^3	55.2	2.70 x 10^3	55.2



(a) Results based on the assumption that CH has been leached from both mortar and the ITZ



(b) Results based on the assumption that CH has been leached solely from mortar in the specimen



(c) Results based on the assumption that CH has been leached solely from the ITZ in the specimen

Figure 3. Comparison of plots showing axial stress versus axial strain for concrete microstructure (with 40 % coarse aggregate) at different levels of degradation caused by CH leaching for 0 d, 28 d and 60 d, subjected to uni-axial compression. Model was fitted to unleached data at 0 d and then used to predict the leached data at 28 d and 60 d with three different sets of assumptions.

leaching in concrete is not very appropriate. It can also be observed from Figure 3 that the strengths are over-predicted when it is assumed that the CH is removed entirely from mortar or that it is removed from both the ITZ and mortar in quantities proportional to their volume (area) fraction in the specimen (microstructure) and that the strengths are under-predicted when it is assumed that CH is leached out from the ITZ only. Under the scenario with the assumption that the CH is removed from both the ITZ and mortar in quantities proportional to their volume (area) fraction in the specimen (microstructure), the extent of leaching in the ITZ is almost 67 % less compared to that in the mortar and hence the effect of leaching on density and thereby stiffness via leaching in the ITZ is very minimal comparatively. Therefore, the response of concrete under this scenario is very similar to that when it is assumed that the CH is removed entirely from mortar as shown in Figures 3(a) and 3(b).

Based on the results obtained for the above three cases and the possibility that the concentration of the external leaching agent is likely to be higher near the surface, it is likely that leaching occurs primarily in the regions closer to the boundaries. Therefore, a simulation was carried out based on the hypothesis that CH is leached from the ITZ and the mortar portions close to the outer boundaries, as shown in Figure 4. It is assumed that an increase in total porosity by 4 % from day 0 to day 28 would mean 2 % of porosity increase due to leaching in the entire ITZ and 2 % increase due to

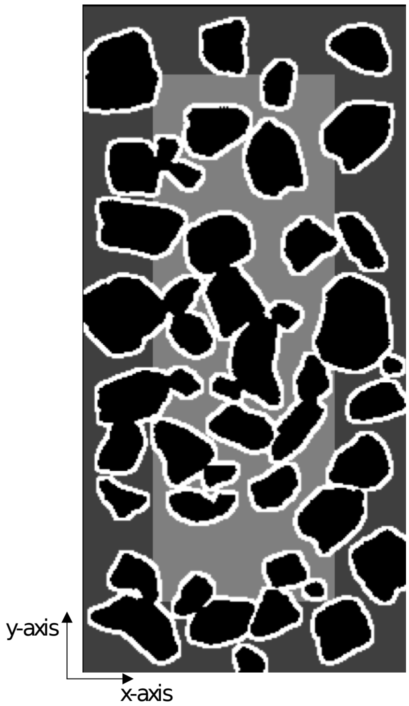


Figure 4. Microstructure used for simulating leaching of CH from mortar that is close to the outer boundaries. CH is preferentially leached from mortar, which is part of the mortar portions in darker gray while there is no leaching in mortar shown in lighter gray.

Table 4. Material properties at three stages of leaching when it is assumed that CH is leached out of the entire ITZ and mortar close to the outer boundaries

	No Leaching		28-day Leaching		60-day Leaching	
Component	Reference Density, kg/m^3	Young's Modulus (E_R), GPa	Reference Density, kg/m^3	Young's Modulus ($E_{R-Leached}$), GPa	Reference Density, kg/m^3	Young's Modulus ($E_{R-Leached}$), GPa
Mortar	2.20 x 10^3	36.0	2.06 x 10^3	29.6	1.92 x 10^3	24.1
ITZ	1.10 x 10^3	12.0	0.880 x 10^3	6.10	0.660 x 10^3	2.60
Aggregate	2.70 x 10^3	55.2	2.70 x 10^3	55.2	2.70 x 10^3	55.2

leaching of the mortar close to the external surface. The same assumption is used for leaching at 60 d. This assumption is based on the idea that this scenario should be almost mid-way between the two cases– one where CH is leached from both the ITZ and mortar proportional to their volume fractions in the microstructure and the second where CH is leached only from the ITZ. The resulting material properties for the three phases of the microstructure are shown in Table 4. The model predicted stress-strain responses are compared with the experimental observations of Huang and Qian as shown in Figure 5. It shows that the model could reasonably predict the effect of leaching on strength, that is, the reduction in strength due to leaching as predicted by model is very close to the reduction observed experimentally. On the contrary, the model-predicted reduction in stiffness due to leaching is much higher than the reduction observed experimentally.

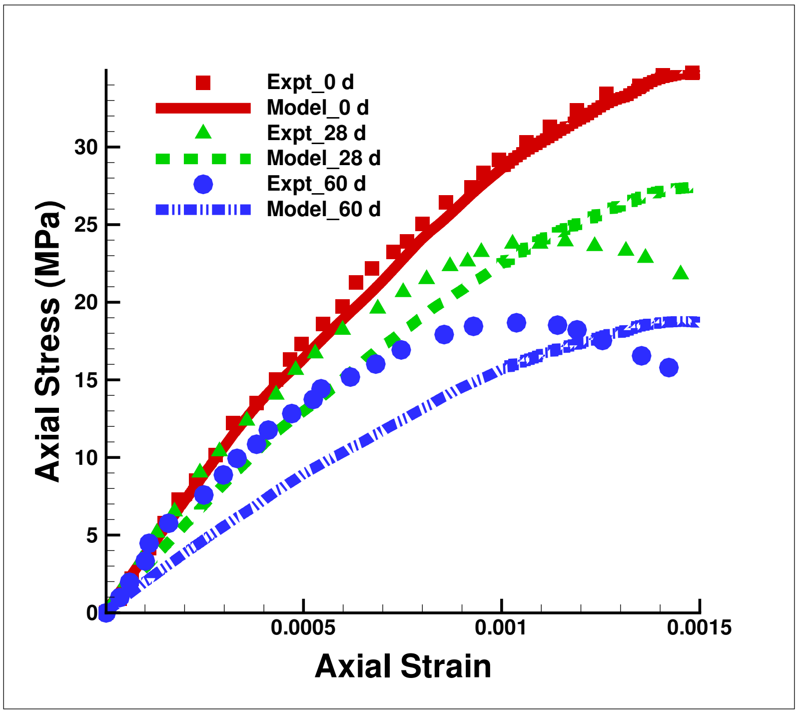


Figure 5. Comparison of plots showing axial stress versus axial strain for concrete microstructure (with 40 % coarse aggregate) at different levels of degradation caused by CH leaching for 0 d, 28 d and 60 d subjected to uni-axial compression, based on the assumption that CH is leached from the entire ITZ and mortar that is close to external surfaces. Model was fitted to unleached data at 0 d and then used to predict the leached data at 28 d and 60 d.

Table 5. Material properties of the three components for the coupled loading scenario

Component	Reference Density, kg/m^3	Young's Modulus (E_R), GPa	Poisson's Ratio (ν)
Mortar	2.20 x 10^3	36.0	0.200
ITZ	1.10 x 10^3	12.0	0.200
Aggregate	2.70 x 10^3	55.2	0.250

3.2. *Concrete subjected to Leaching and Uni-axial Compression Loading Simultaneously*

In this section, the response of concrete subjected to uni-axial compressive loading as it is being leached is predicted. In a scenario where concrete is subjected to mechanical load as it is exposed to leaching, density (porosity) changes simultaneously due to two factors: i) mass reduction- leaching of calcium hydroxide from the matrix leading to creation of empty spaces (pores) ii) volume increase- volumetric strains caused by stresses developed locally due to mechanical loading. When chemical leaching and mechanical loading act simultaneously on the material, the density of each phase (i = ITZ, mortar) at any instant during the loading is evaluated using Eq.(16). Then, this density expression is substituted in the constitutive equation given by Eq.(17), which is used to model the response of concrete to the coupled loading. In this case, a value of 0.001 is used for γ.

Three cases are considered for this simulation, as in Sec 3.1. The reference values of density and Young's modulus are as shown in Table 5.

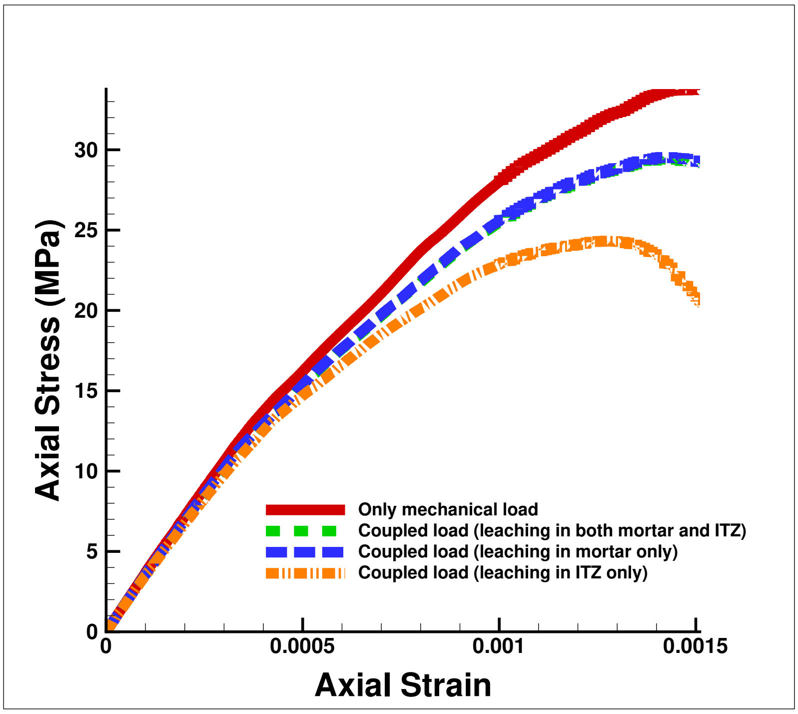


Figure 6. Comparison of concrete's responses to scenario of coupled loading where leaching and uni-axial compressive loading act simultaneously and to that of pure uni-axial compression. Three cases are further considered under coupled scenario- CH leaching from both mortar and the ITZ, CH leaching only from mortar and CH leaching from only the ITZ. Coupled loading implies that concrete is subjected to leaching and uni-axial compression simultaneously for the entire loading period.

As the microstructures in all three cases are being leached, they are also subjected to uni-axial compression as described earlier in this section, such that there is simultaneous application of mechanical and chemical load. The response of concrete in these three cases is compared with a scenario where the material is subjected to the same uni-axial compressive load but without any exposure to leaching. The comparison is shown in Figure 6. This figure shows that in a coupled loading scenario where the material is subjected to both leaching and uni-axial compression, the model-predicted deterioration in the material is greater compared to a scenario where the material is subjected solely to uni-axial compression. Here, deterioration refers to a reduction in both strength and stiffness of the material. Additionally, the model-predicted response to the coupled loading, in all three cases, is compared to that under a scenario of superposed chemical-mechanical loading (leaching is followed by uni-axial compression without any overlapping of the two loadings) as shown in Figure 7. It can be observed in the figure that the two responses are not identical, implying that it is not appropriate to determine the response of the material subjected to chemical leaching and mechanical loading simultaneously by superposing the responses to independently acting chemical and mechanical loads without considering overlap.

3.3. *Discussion*

The results for the scenario where concrete is first leached and then subjected to uni-axial compression, presented in Figure 3, show that there is material deterioration in the form of strength and stiffness reduction, both by around 28-88 %, over the

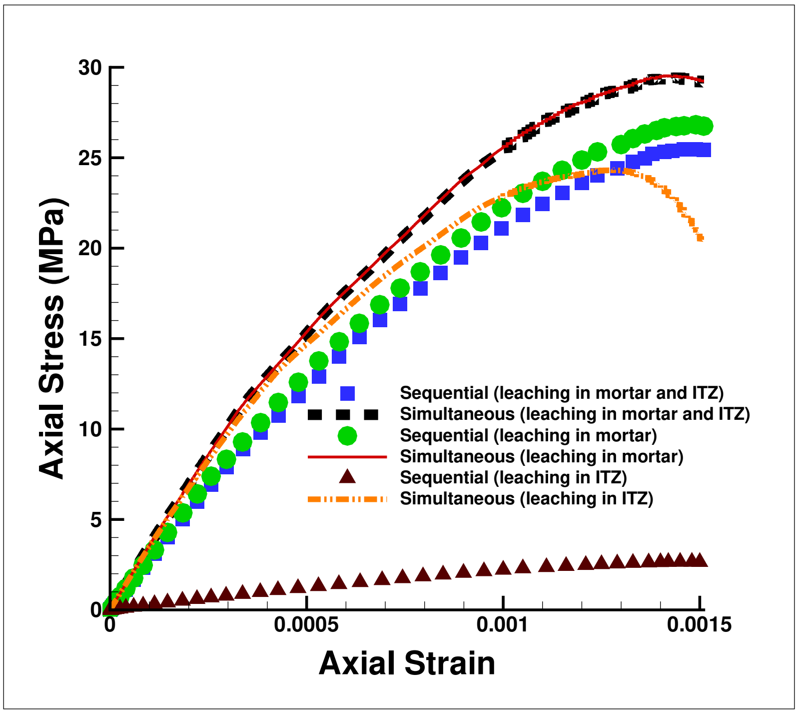


Figure 7. Comparison of concrete's response to scenario of coupled loading where leaching and uni-axial compressive loading act simultaneously to a response obtained by superposing the responses to independently acting leaching and uni-axial compression (without overlapping)- the former scenario is referred to as simultaneous (degradation) and the latter as sequential (degradation). Three cases are further considered under the coupled scenario- CH leaching from both mortar and the ITZ, CH leaching only from mortar and CH leaching from only the ITZ. Superposition of leaching and uni-axial compression implies that concrete is first exposed to leaching and then subjected to uni-axial compression when the leaching process is completed.

course of loading (both chemical followed by mechanical). The degradation in the form of stiffness reduction caused by the processes of both leaching and uni-axial compression is a result of the density changes shown in Eqs.(18), (19) and (17). While leaching caused density reduction through creation of porosity, uni-axial compression leads to density reduction through localized volumetric expansion. When concrete is subjected to uni-axial compression, the material tends to get denser when observed at a macroscopic level, but there are some local areas (mainly in the ITZ regions) where the density drops due to local tensile strains (stresses) in the lateral direction (direction perpendicular to that of loading) (Murru *et al.* Under review). As mentioned earlier, CH could be removed from either or both of the ITZ and mortar and it is almost impossible to determine what amounts of CH are removed from each of these phases. Based on the results obtained, it is clear that the strengths are over-predicted when it is assumed that the CH is removed entirely from mortar or that it is removed from both mortar and the ITZ. On the other hand, the strengths are under-predicted when it is assumed that CH is leached out solely from the ITZ. Therefore, it is most likely that CH is removed from both the ITZ and mortar, but with the larger contribution being from the ITZ phase. That is, it is likely that CH leached from the ITZ is significantly more than a sixth (volume fraction of ITZ among the components from which CH could be leached– ITZ and mortar) of the total CH leached due to leaching. In alignment with this inference, a simulation was carried out such that CH was leached out from the entire ITZ and the mortar only close to the external surface. Though this could manage to reasonably predict strengths (and drop in strengths due to leaching), the stiffness values are under-predicted (or the drop in stiffness due to leaching is over-predicted), as discussed earlier in this section with the help of Figure 5. In reality, there would be local regions where there is concentrated damage, which would lower the strength without significant reductions in stiffness (as observed experimentally) (Kaplan 1961).

In case of the coupled chemical and mechanical loading scenario, concrete is subjected to uni-axial compression as it is being chemically leached. It would be expected that the material degradation in this case is greater than in the case where concrete is subjected to pure uni-axial compression as there would be density reduction due to both leaching and volumetric expansion caused by mechanical loading. This is supported by the model-predicted results shown in Figure 6, which indicate that the reduction in strength and stiffness of the material under coupled loading, as predicted by the D3-M model, is greater compared to a scenario where the material is subjected solely to uni-axial compression. In addition, the response to a coupled loading scenario cannot be considered equivalent to the superposition of independent responses to chemical and mechanical loading. This is evident from the comparison of the model-predicted results shown in Figure 7, which prove that the two responses are not identical. It shows that the strength and the stiffness predicted by the model for a coupled scenario are close to 12 % higher than the strength and the stiffness predicted under a superposed scenario, when it is assumed that leaching occurs in both mortar and the ITZ or that it occurs in mortar only. This implies that the response of the material subjected to coupled loading cannot be determined by simply superposing the responses to independently acting chemical and mechanical loads. Thus, when modeling concurrent chemical and mechanical degradation of concrete- as often happens in real structures- it is necessary to use a fully coupled, fully consistent modeling framework as was presented here.

4. Conclusion

The modeling of damage in concrete due to chemical attack only or due to a combination of chemical and mechanical loads has been a challenging task. Researchers in the past have tried to use models where the chemical damage parameter is defined using parameters such as calcium ion concentration or depth of the degraded zone, and the mechanical damage is defined as a function of quantities like stresses and strains whose initial values in the body under consideration are not known. In some cases, the two damage types are looked at as independently acting phenomena such that one can superpose the two damage parameters defined separately using mechanical and chemical attributes. In order to attribute physical significance to the models used to predict the chemical and coupled chemo-mechanical damages, the choice of a real, measurable parameter – density – to quantify damage was considered apt. Hence, an implicit constitutive model (D3-M model), which defines damage in terms of density changes, was chosen to simulate the chemical and chemo-mechanical responses of concrete. It is of importance that the D3-M model is able to predict the response of concrete due to mechanical damage (Murru *et al.* Under review), chemical damage as well as damage due to coupled mechanical-chemical loads, using the same form of constitutive equation developed based on the theory that microscopic changes in density lead to the damage (mechanical, chemical or chemo-mechanical) in the material. In the current study, the behavior of a simple 2D concrete model was analyzed using D3-M to predict the response under two scenarios- one where leached concrete is subjected to uni-axial compression and the other where concrete is subjected to uni-axial compression as it is being leached. The coupled chemo-mechanical model is able to predict the experimentally observed trend in reduction of stiffness and strength of concrete when it is subjected to uni-axial compression at different levels of chemical degradation. Although the trends could be predicted, the exact strength loss in terms of magnitude could not be matched under the different scenarios with various assumed levels of contribution to leaching from the ITZ and mortar phases. This could be because of the uncertainty in the distribution of porosity induced by leaching across the phases of mortar and the ITZ, and the fact that the model was only 2D. In addition, it can be observed from the figures presenting a comparison between the experimental data and the model predicted responses (Figures 3 and 5) that there is some non-linearity over the course of the loading. Therefore, an infinitesimal strain based model, which assumes a linear dependence of stiffness on density changes, might not have ably captured the stiffness reductions.

Unlike most of the existing approaches to model chemical damage in concrete, the D3-M model is able to clearly distinguish between the scenarios of superposition of independent chemical and mechanical responses and of coupling of simultaneous chemical and mechanical responses. To the knowledge of the authors, D3-M is the first modeling framework to capture this difference, since it is the first to use a consistent damage framework for both chemical and mechanical degradation of concrete.

Acknowledgements

Portions of this research were conducted with the advanced computing resources provided by Texas A&M High Performance Research Computing.

Disclaimers

Certain commercial equipment, instruments, or materials (MATLAB, OOF2 and ABAQUS) are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

References

Abaqus Users Manual, 2013. *Version 6.13-2*. Available from: http://dsk.ippt.pan.pl/docs/abaqus/v6.13/index.html.

Bangert, F., *et al.*, 2003. Environmentally induced deterioration of concrete: physical motivation and numerical modeling. *Engineering Fracture Mechanics*, 70 (7-8), 891–910.

Carde, C. and François, R., 1997a. Aging damage model of concrete behavior during the leaching process. *Materials and Structures*, 30 (8), 465–472.

Carde, C. and François, R., 1997b. Effect of the leaching of calcium hydroxide from cement paste on mechanical and physical properties. *Cement and Concrete Research*, 27 (4), 539–550.

Coussy, O., 1995. *Mechanics of porous continua*. Hoboken, NJ: Wiley.

Diamond, S. and Huang, J., 2001. The itz in concrete–a different view based on image analysis and sem observations. *Cement and Concrete Composites*, 23 (2), 179–188.

Gérard, B., 1996. *Contribution of the mechanical, chemical and transport couplings in the long term behavior of radioactive waste repository structures*. Thesis (PhD). Laval University, Québec, Canada–Ecole Normale Supérieure de Cachan, France.

Grasley, Z.C. and Rajagopal, K.R., 2012. Revisiting total, matric, and osmotic suction in partially saturated geomaterials. *Zeitschrift für angewandte Mathematik und Physik*, 63 (2), 373–394.

Huang, B. and Qian, C., 2011. Experiment study of chemo-mechanical coupling behavior of leached concrete. *Construction and Building Materials*, 25 (5), 2649–2654.

Jebli, M., *et al.*, 2018. Leaching effect on mechanical properties of cement-aggregate interface. *Cement and Concrete Composites*, 87, 10–19.

Kaplan, M., 1961. Crack propagation and the fracture of concrete. *Journal of the American Concrete Institute. Proceedings*, 58 (11), 591–610.

Kuhl, D., Bangert, F., and Meschke, G., 2000. An extension of damage theory to coupled chemo-mechanical processes. *In*: *European Congress on Computational Methods in Applied Sciences and Engineering (ECCOMAS), Barcelona, Spain.*

Langer, Reid, and Dogan, 2017. *Oof: Finite element analysis of microstructures*. Available from: https://www.ctcms.nist.gov/oof/oof2/.

Langer, S.A., *et al.*, 2008. *The OOF2 manual*. Available from: https://www.ctcms.nist.gov/ langer/oof2man/.

Le Bellégo, C., *et al.*, 2003. Coupled mechanical and chemical damage in calcium leached cementitious structures. *Journal of Engineering Mechanics*, 129 (3), 333–341.

MatLab, M., 2012. The language of technical computing. *The MathWorks, Inc. http://www. mathworks. com.*

Mazars, J., 1984. *Application de la mécanique de l'endommagement au comportement non linéaire et à la rupture du béton de structure*. Thesis (PhD). Universite Pierre et Marie Curie-Paris 6.

Murru, P.T., *et al.*, Under review. Density driven damage mechanics (D3-M) model for concrete I: mechanical damage. *International Journal of Pavement Engineering.*

Prasad, S.C. and Rajagopal, K.R., 2006. On the diffusion of fluids through solids undergoing large deformations. *Mathematics and Mechanics of Solids*, 11 (3), 291–305.

Qian, Z., *et al.*, 2016. Anm: a geometrical model for the composite structure of mortar and concrete using real-shape particles. *Materials and Structures*, 49 (1-2), 149–158.

Rajagopal, K., 2007. The elasticity of elasticity. *Zeitschrift für angewandte Mathematik und Physik*, 58 (2), 309–317.

Scrivener, K.L., Crumbie, A.K., and Laugesen, P., 2004. The interfacial transition zone (itz) between cement paste and aggregate in concrete. *Interface Science*, 12 (4), 411–421.

Spencer, A.J.M., 2004. *Continuum mechanics*. Chelmsford, Massachusetts, USA: Courier Corporation.

Tao, L., Humphrey, J., and Rajagopal, K., 2001. A mixture theory for heat-induced alterations in hydration and mechanical properties in soft tissues. *International Journal of Engineering Science*, 39 (14), 1535–1556.

Ulm, F.J., Torrenti, J.M., and Adenot, F., 1999. Chemoporoplasticity of calcium leaching in concrete. *Journal of Engineering Mechanics*, 125 (10), 1200–1211.

Vichit-Vadakan, W. and Scherer, G.W., 2002. Measuring permeability of rigid materials by a beam-bending method: III, Cement Paste. *Journal of the American Ceramic Society*, 85 (6), 1537–1544.

Young, J.F., Mindess, S., and Darwin, D., 2002. *Concrete*. Upper Saddle River, NJ, USA: Prentice Hall.