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Examination of Gamma-irradiated Calcium Silicate Hydrates. Part II: Mechanical Properties

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Abstract

Mechanical properties of calcium silicate hydrates (C-S-H) with C/S ratios of 0.75, 1, and 1.33 were examined with nanoindentation after gamma-adsorbed doses of 0.145, 0.280, 0.500, and 0.784 MGy, and were compared with control samples. Young's modulus and stress relaxation tests showed no apparent trend with irradiation dose. Qualitatively, most of the irradiated samples were found to relax more than their respective controls, but not always in a statistically significant manner. Most of the Young's modulus irradiated-control pairs showed marginally higher stiffness in the irradiated samples, but overall trends with irradiation dose were not obvious. Creep compliance was obtained for the samples irradiated at the highest dose and their respective controls. Two of the three irradiated samples exhibited less creep than their respective controls, but only one of which was statistically significant. The lack of clear changes in mechanical properties for these samples correlates with separate chemical analyses that showed no loss of interlayer water by exposure to irradiation or changes in the mean silicate chain length. Further research evaluating higher doses (25 and 200 MGy) representative of those received by concrete structures in nuclear power plants at prolonged operation is being carried out to complement the present study.

1. Introduction

Concrete, which is composed of cement and aggregates, is the most used construction material worldwide. Among its numerous applications are those related to radiation shielding in the biological shields of light water reactors (LWRs). These shields protect against neutrons and gamma rays exiting the reactor pressure vessel (RPV). In some pressure water reactor (PWR) designs, the biological shield also fulfills a structural function by supporting the RPV. As such, the concrete in the biological shield must not degrade under the unique environmental conditions. Many utilities in the United States are considering extending the operational phases of LWRs for up to 80 years (second license renewal). Such an extension would lead to concrete in these facilities receiving unprecedented irradiation exposures to neutron fluxes up to 7.0×10^{19} n/cm² ($E > 0.1$ MeV) (Remec 2014; Field *et al.* 2015) and gamma ray doses of 50 to

200 MGy (Esselman *et al.* 2013; Kontani *et al.* 2013; Remec 2013), requiring reassessment of the long-term integrity of the affected structural members.

Fast neutrons ($E > 10$ keV) cause the amorphization of minerals present in aggregates, leading to radiation-induced volumetric expansion (RIVE) (Kontani *et al.* 2013; Field *et al.* 2015; Le Pape *et al.* 2015; Remec *et al.* 2017), whereas gamma rays cause radiolysis that leads primarily to the decomposition of cement paste water (Kontani *et al.* 2013; Field *et al.* 2015). Chemically bound water can be decomposed, although it has been reported that only less than 1.5% (Kontani *et al.* 2013) or 2 to 3% (Ishikawa *et al.* 2019) of the chemically bound water is lost for pre-dried cement pastes at 120°C after exposure to 200 MGy. RIVE-induced stresses created in the hardened cement paste can be dissipated either by cracking or by relaxation (Giorla *et al.* 2015; Le Pape *et al.* 2015). Following accelerated irradiation experiments in test reactors, the mechanical properties of irradiated concrete can considerably decrease (Field *et al.* 2015). The irradiation flux for concrete in LWRs is about 1 to 3 orders of magnitude lower than in test reactors (Maruyama *et al.* 2013; Remec *et al.* 2016), suggesting the possibility of relaxation mechanisms delaying the onset of irradiation-induced damage. In fact, a recent physics-based predictive model for neutron-irradiation damage in concrete suggests a delay in the onset of irradiation damage when creep is present in both free and restrained concrete (Giorla *et al.* 2015, 2017). Creep was considered independent of fluence in this model. The in-situ effect of both neutron and gamma irradiation on concrete creep has received little attention in past research, but the limited available data suggest that creep kinetics are altered during irradiation (Gray 1971). A study that

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separates the effects of neutrons and gamma rays on concrete creep is still lacking. The exposure to gamma rays may influence the relaxation behavior of cement paste due to dehydration. The literature on the creep of gamma-irradiated cementitious systems is particularly scarce, but it suggests a reduction in creep rate for concrete, even after exposure to only 0.8 MGy (McDowall 1971). A reduction in creep was also observed in mortars irradiated to 0.257 MGy (Hilloulin *et al.* 2018). This needs to be investigated further with both in-situ coupled irradiation creep experiments and post-irradiation studies of stress relaxation and creep in cement paste.

The viscous response of cement paste originates primarily from C-S-H, the main hydration phase. The rate of C-S-H creep largely exceeds those of other hydrated phases and thus dominates the creep behavior in cement and concrete. The underlying mechanisms of C-S-H creep are still not fully understood, but the viscoelastic or viscoplastic slide of particles, blocks, and/or sheets with respect to each other (Lynam 1934; Thomas 1937; Ulm *et al.* 1999; Tamtsia and Beaudoin 2000; Acker 2004; Jennings 2004; Vandamme and Ulm 2009; Alizadeh *et al.* 2010; Morshedifard *et al.* 2018; Vandamme 2018), or the stress-induced dissolution mechanisms (Pignatelli *et al.* 2016; Li *et al.* 2018; Moradian *et al.* 2018) are the most common propositions: both mechanisms result in the structural reorganization of C-S-H in order to relax stress. A new speculative model of C-S-H growth envisions a type of bond in between C-S-H sheets in which calcium ions bridge between oxygen atoms in silicate groups (Gartner *et al.* 2017). It was suggested that creep could be caused by the movement of these bonds from one site to another due to stress and/or thermal activation. The stress relaxation of C-S-H depends on its water content: fully saturated specimens exhibit a hydrodynamic relaxation component caused by water moving through the pore network when stress is applied, whereas samples dried to 11% relative humidity (RH) and further do not exhibit the hydrodynamic behavior, and the viscous response is a result of deformations of the solid body (Alizadeh *et al.* 2010). Interlayer water has also been shown to play an important role in the viscous response of C-S-H, as partial removal of interlayer water lowers the stress relaxation response (Alizadeh *et al.* 2010). The viscous response of C-S-H also depends on its chemical structure, as well as its elastic properties (Alizadeh *et al.* 2010, 2011; Hunnicutt *et al.* 2016). Increasing the C/S ratio causes the mean silicate chain length (MCL) to decrease, thus increasing the number of sliding blocks per gram of material to yield a more viscous response. The effect of silicate polymerization of C-S-H on creep was observed by others studying C₃S pastes cured at high temperatures (Bentur *et al.* 1979). Pastes cured at high temperatures contained more polymerized C-S-H and exhibited less creep. Studies of creep of using nanoindentation indicate that creep behavior during nanoindentation closely correlates with long-term macroscopic creep behavior in cementitious materials (Vandamme and Ulm 2013;

Vandamme 2018). Recently, stress relaxation nanoindentation experiments have been used to probe the viscoelastic response of synthetic C-S-H and C-(A)-S-H with C/S = 1 and Al/Si = 0.2 (Hunnicutt *et al.* 2016). The results suggest that C-(A)-S-H was less viscous than C-S-H given its longer mean aluminosilicate chain length and the presence of cross-linking silicate tetrahedra between the main layers, which were thought to offer more resistance to the sliding of particles under load.

With the purpose of providing data to further extend and develop irradiation damage prediction models for concrete, the viscoelastic response of C-S-H with C/S ratios of 0.75, 1, and 1.33 after gamma ray doses of 0.145, 0.280, 0.500, and 0.784 MGy was tested with stress relaxation nanoindentation, and the results were compared with the response of non-irradiated samples. Young's modulus was also obtained through nanoindentation for all samples, and creep compliance curves were obtained for the samples irradiated at the highest dose and their respective controls. The samples were preconditioned to 11% RH to eliminate the hydrodynamic component arising from pore water and to study the stress relaxation purely due to deformations of the solid body of C-S-H. At 11% RH, C-S-H is considered to have a monolayer of water molecules adsorbed in surfaces and chemically bound water in the interlayer (Feldman and Ramachandran 1974; Alizadeh *et al.* 2010). Chemical structural analyses of the samples suggested that all interlayer water remained after irradiation; no changes were found in morphology, C/S ratio, or silicate anion structure, and the C-S-H was phase-pure; there are no significant changes in the chemical structure of the C-S-H at the irradiation doses up to 0.784 MGy (Tajuelo Rodriguez *et al.* 2020). Testing different compositions (C/S ratios) also provides information about how changes in the chemical structure could potentially alter the effects of the irradiation on the viscous response. In fact, it has been shown that interlayer water has a more significant structural role in high C/S C-S-H than in low C/S C-S-H since the viscous response in high C/S C-S-H is more prone to changes after drying to below 11% RH (Alizadeh *et al.* 2010). Previously, a reduction of creep rate was reported for concrete irradiated at 0.8 MGy and for mortars irradiated at 0.257 MGy (Hilloulin *et al.* 2018); a drop in the viscous response was expected to occur in the current experiments, and the magnitude of this drop may depend on the chemical structure of the samples. Other properties related to the stability of C-S-H depend on its chemical composition. For example, C-S-H with a low C/S ratio is less prone to calcium leaching (Gaitero *et al.* 2009) and more thermally stable than C-S-H with high C/S ratios (Tajuelo Rodriguez *et al.* 2017).

2 Materials and methods

2.1 Synthesis of C-S-H and pellet preparation

An abbreviated summary of C-S-H synthesis is provided

here; the full details are presented elsewhere (Tajuelo Rodriguez *et al.* 2020). C-S-H was synthesized by mixing SiO₂ (Aerosil 200) and CaO with C/S ratios of 0.75, 1, and 1.33. The reactants were mixed in 1 L high density polyethylene bottles with deionized water at a water to solid ratio of 8 in an inert atmosphere. They were milled for two days following the mechanochemical synthesis procedure (Saito *et al.* 1997; Garbev *et al.* 2008). The bottles were opened in a glovebox to prevent the carbonation of the slurries. The slurries were dried at 50°C under nitrogen, crushed and sieved, and then conditioned at 11% RH. Pellets were pressed with 2 g of powder each with a 250 kN load in a 50-ton hydraulic press to produce pellets that are 25.4 mm (1 inch) in diameter and approximately 2 mm (0.08 in) thick. The piston of the die used to compact the pellets had a polished surface that imprinted a smooth and flat surface onto the C-S-H pellets that is suitable for nanoindentation measurements (Hunnicutt 2018). This compaction method for C-S-H has been shown to provide mechanical properties that approximate those of hydrated cement (Feldman 1972). The pellets were stored at 11% RH for two weeks before irradiation.

2.2 Gamma irradiation

The irradiation experiments were conducted using a Co⁶⁰ gamma reactor (J. L. Shepherd Model 109-68 Co⁶⁰ unit). The pellets were irradiated in sealed stainless-steel containers under a flow of argon of 0.15 slpm. The samples were irradiated to absorbed gamma doses of 0.145, 0.280, 0.500, and 0.784 MGy. More information about dose rate calculations can be found in a paper by Tajuelo Rodriguez *et al.* (2020). The low dose rate of the reactor allowed for room temperature to be maintained during irradiation. Control samples were stored in replicated sealed containers and connected to the same argon flow outside of the radiation chamber. A section of the pellets was glued to an Atomic Force Microscopy (AFM) specimen disc (Ted Pella, Inc.) for nanoindentation after irradiation. Samples were stored in a constantly low-flowing nitrogen-filled glovebox to avoid carbonation until nanoindentation experiments were conducted. A petri-dish with soda-lime was placed in the indenter chamber to avoid carbonation during testing.

2.3 Nanoindentation

The nanoindentation experiments were performed using a Hysitron Triboindenter equipped with a diamond Berkovich tip. A 10 × 10 grid with 5 μm spacing between indents was used for stress relaxation and creep nanoindentation. For stress relaxation nanoindentation, a displacement of 175 nm was achieved in 1 s. The tip was held at this displacement for 120 s and was unloaded in 1 s. This load function provides an approximate step function for displacement that is assumed for convenience during the analysis. During method development it was determined that a 1 s loading time is the fastest the sample could be reliably loaded (Hunnicutt 2018). A fast load

rate was desired to better approximate a step loading function, especially since there appears to be significant relaxation at early times. The displacement of 175 nm was chosen according to previous tests with dynamic nanoindentation, which indicated that deeper displacements gave rise to non-linear viscous phenomena. The thermal drift was minimized by using the piezo automation function of the indenter and putting the tip in contact with the sample for at least 3 hours before the indentation started to allow the non-piezo motors to settle. The settling time used between indents was 1 minute to allow for piezo relaxation. The displacement function was approximated to a step function because the indentation equation has a very simple solution (in the case of a time-independent Poisson's ratio) in which the normalized force (P) is equal to the normalized relaxation modulus (E) and is independent of porosity (Cao *et al.* 2010):

$$\frac{P(t)}{P_0} = \frac{E(t)}{E_0} \quad (1)$$

Stress relaxation nanoindentation was chosen as the ideal experimental method to compare C-S-H pellets with different C/S and irradiation doses since the normalized stress relaxation modulus is independent of porosity (Cao *et al.* 2010), thus eliminating a variable that is difficult to control. Note that prior to normalization, the stress relaxation modulus is not independent of porosity and is related to the creep compliance. The curves for force vs. time were entered into a MATLAB code to obtain the normalized force. The high load occurring during the beginning of the hold was used to normalize the force. The curves in which the force was increasing with time were discarded by visual inspection, and then a criterion was applied to discard other erroneous curves if: drift > 0.2 nm/s, force at 50 s > force at 10 s, or force at 100 s > force at 20 s.

A bias-corrected and accelerated bootstrap statistical analysis (Efron and Tibshirani 1994) was performed on the accepted normalized force curves to create mean curves with 95% confidence intervals ($\alpha = 0.05$). The C-S-H pellets are phase-pure and the statistical analysis presented will capture local variability in porosity and nanostructure, the indentation grid allows for the assumption that each indent is an independent measurement. The analysis took data every tenth time step and randomly sampled for every time step, creating 2000 data sets from the original data which were used to calculate the statistics. The advantage of bootstrap statistics over traditional statistical methods is that the probability distribution function is empirical and is not required to be normal (Efron and Tibshirani 1994). The mean curve of the generated data was considered the best measure of central tendency and was fitted with a Prony series. The Prony series representation of the relaxation modulus is:

$$E(t) = E_{\infty} + \sum_{i=1}^N E_i \exp(-t / \tau_i) \quad (2)$$

where t = time, τ = relaxation time, and E_∞ = long-term modulus. E_∞ is unknown but can be expressed in terms of E_0 :

$$E_\infty = E_0 - \sum_{i=1}^N E_i \quad (3)$$

Then the normalized relaxation modulus can be expressed as

$$\frac{E(t)}{E_0} = 1 - \sum_{i=1}^N \frac{E_i}{E_0} [1 - \exp(-t/\tau_i)] \quad (4)$$

This expression was used to fit the mean data starting with a two-term series and adding terms until the error (difference with the bootstrap mean) was less than 0.2%.

Creep nanoindentation measurements were performed in a similar fashion as stress relaxation with a 10×10 grid of indentations and $5 \mu\text{m}$ spacing. A load of $1000 \mu\text{N}$ was achieved in 1 s, and the tip was held at this load for 120 s and was unloaded in 1 s. Unlike the stress relaxation experiments, the creep compliance is not independent of porosity. The thermal drift was minimized using the piezo automation function of the indenter and putting the tip in contact with the sample for at least 3 hours before the indentation started to allow the motors to settle. The settle time used between indents was 1 minute. Raw time and displacement data were imported and analyzed using MATLAB. The curves in which the displacement was decreasing with time were discarded based on visual inspection, and then a criterion was applied to discard other erroneous curves. The criterion applied was: drift $> 0.2 \text{ nm/s}$, displacement at 50 s $<$ displacement at 10 s, or displacement at 100 s $<$ displacement at 20 s.

A bootstrap statistical analysis was performed on the creep data to create 95% confidence intervals in the same manner as the stress relaxation analysis. Displacement data were fit to a function that allows for determination of the creep compliance (Jones and Grasley 2011):

$$h(t) = 1.21 \sqrt{P_{\max}(J(t)) \cot \theta} \quad (5)$$

where $P_{\max}$ is the max load, $J(t)$ is the creep compliance as a function of time, and θ is the equivalent half-angle of the indenter tip. The creep compliance function is taken in the form of a stretched exponential function:

$$J(t) = \frac{1}{E_0} + \frac{1}{E_i(1-e^{-1})} \left(1 - e^{-(t/t_h)^\beta}\right) \quad (6)$$

where E_0 controls the elasto-plastic response, E_i controls the time dependent response, β controls the shape of the time dependent response, and t_h is the hold time. E_0 is determined by the initial loading depth using the solution for an axisymmetric Boussinesq indentation problem (Sneddon 1965) and the conversion from reduced modulus (also referred to as the indentation modulus) to elastic modulus assuming an infinitely stiff indenter tip:

$$h^2(t) = \frac{\pi P(t)}{2 \tan \theta(E_r)} \quad \text{and,} \quad (7)$$

$$E = E_r(1-\nu^2) \quad (8)$$

where $h(t)$ is the displacement as a function of time, $P(t)$ is the load as a function of time, θ is equivalent half-angle of the indenter tip, E_r is the reduced modulus of the sample, E is the Young's modulus of the sample, and ν is the Poisson's ratio of the sample (0.2). E_i and β are solved for by fitting the mean time-dependent displacement data in the equation mentioned above for $h(t)$.

The elastic response was tested reaching a load of $4000 \mu\text{N}$ in 5 s, holding it for 5 s, and unloading in 5 s. A 10×20 grid with $10 \mu\text{m}$ spacing was used, with a settle time of 1 minute between indents. The reduced modulus (E_r) was computed from the unloading curves (load vs. displacement) by the instrument software using the Oliver-Pharr method. Curves with drifts greater than 0.2 nm/s , and those with kinks in the loading section were rejected to calculate the Young's modulus (E). The Poisson's ratio was assumed to be 0.2. The mean Young's modulus with 95% confidence intervals ($\alpha = 0.05$) was calculated in a manner similar to that used to calculate the stress relaxation and creep data using bias-corrected and accelerated bootstrap statistical analysis. The Young's modulus from every accepted indent was randomly sampled, creating 2000 data sets from the original data, which were used to calculate the statistics.

To determine whether samples were significantly different from each other for each experiment type, a statistical test was devised based on the bootstrap method described above. To establish whether the samples were equivalent, a distribution of the difference in mean between samples was constructed; if the 95% confidence interval contained zero, then there was no significant difference between the means of the two samples. The distribution of the difference between the means must be used to compare data instead of simply comparing the confidence intervals of the two samples due to how error is calculated in these two methods. When comparing overlapping confidence intervals (based on the distribution of the mean), the total error is the linear sum of the two mean distributions; this method of summing the error overestimates the uncertainty. Uncertainty of differences in random, independent samples propagates as the square root of the sum of squares, which will always be less than the linear sum. Therefore, comparing overlapping confidence intervals results in greater, and incorrect, uncertainty than estimating the uncertainty via the difference in mean of the two data sets. By using the distribution of differences, uncertainty is estimated correctly. When conducting the bootstrap statistical test described above to compare the means of two different samples, equivalent sample sizes are required due to the use of a jackknife calculation in the bias-corrected and accelerated method for calculation of bootstrap statistics (Efron and Tibshirani 1994).

The indent data generated were force and displace-

ment as a function of time. For each time-step, a bootstrap sample was created from the grid of indents. To produce a test for equivalency of indent behavior between irradiated and control samples, the sample sizes must be the same. For this test, the acceleration term was estimated in a conservative fashion, erring on the side of larger uncertainty, by randomly removing indents from the larger data set so that the two resulting data sets had

the same sample size. Typically, the difference in sample size was only a few indents, and most of the data were retained. The data created as a result of the random sampling (displacement for creep, normalized force for stress relaxation, and Young's modulus) were then fitted to appropriate models, and confidence intervals were created. A flow chart of the analysis process is displayed in **Fig. 1**.

Fig. 1 Flowchart for statistical analysis.

Table 1 Results of bootstrap statistical test for equivalence ($\alpha = 0.05$) for stress relaxation curves of control and irradiated C-S-H samples. The number of indents used after reducing the sampling for equal sample size is also indicated after the equivalence.

	CSH 0.75	CSH 1	CSH 1.33
0.145 MGy dose	Not equivalent/74	Not equivalent/75	Not equivalent/62
0.280 MGy dose	Equivalent/72	Not equivalent/84	Not equivalent/50
0.500 MGy dose	Not equivalent/75	Equivalent/81	Not equivalent/70
0.784 MGy dose	Equivalent/90	Equivalent/70	Not equivalent/68

Table 2 Results of bootstrap statistical test for equivalence ($\alpha = 0.05$) for Young's modulus of control and irradiated C-S-H samples. The number of indents used after reducing the sampling for equal sample size is also indicated after the equivalence.

	CSH 0.75	CSH 1	CSH 1.33
0.145 MGy dose	Not equivalent/137	Not equivalent/159	Not equivalent/107
0.280 MGy dose	Equivalent/40	Not equivalent/60	Not equivalent/83
0.500 MGy dose	Equivalent/179	Equivalent/156	Not Equivalent/159
0.784 MGy dose	Equivalent/162	Equivalent/179	Equivalent/175

3. Results and Discussion

Figure 2 shows the fit for the mean normalized stress relaxation data after the bootstrap analysis for all control and irradiated samples.

The results of the bootstrap statistical test for equivalence of the normalized stress relaxation curves for the control and irradiated samples are presented in **Table 1**.

Some of the irradiated–control pairs were equivalent, while some were not. Among the pairs in which the dosed and control samples did not have equivalent mean values of normalized force, a majority of the dosed samples relaxed more than the control samples. The C-S-H 1.33 pair at 2 months (0.145 MGy) and 7.5 months (0.500 MGy) were the exceptions. This can be seen with greater clarity in **Fig. 3**, in which the normalized force at the end of the hold period was plotted against gamma dose for the three C/S ratios. However, it is also evident from **Fig. 3** that the total dose did not have a substantial impact on the normalized force at the end of the hold period since the data showed no visible trend with increasing irradiation doses. The tested irradiation doses do not appear to have an obvious impact on the normalized stress relaxation behavior of the C-S-H samples. It should be noted that the normalized stress relaxation moduli of the control samples stored for different lengths of time before testing displayed in **Fig. 2** do not exhibit the exact same behavior; a specific reason for this discrepancy could not be determined, but a potential explanation involving the relative humidity during storage is given at the end of this section.

The normalized force at the end of the hold period was plotted against the MCL and the degree of cross linking in **Fig. 4**. The data showed no correlation. This contradicts other reported results that claimed a change in creep/viscous behavior with silicate polymerization (Bentur *et al.* 1979; Hirljac *et al.* 1983; Alizadeh *et al.* 2011).

The data presented here also cast doubt on previous observations of a decrease in viscous response with

higher MCL and/or a greater degree of cross-linking from similar stress relaxation tests (Hunnicutt *et al.* 2016). These observations were based on stress relaxation results from two samples: C-S-H with Ca/Si = 1, MCL of about 7 and no cross-linking, and C-(A)-S-H with Ca/Si = 1, Al/Si = 0.2, MCL of about 28 and 11% cross-linking. The present work explored a cross-linking range of 0 to 31% and an MCL range of 2 to 16 (Tajuelo Rodriguez *et al.* 2020), and no change on viscoelasticity was observed. However, an effect of higher MCLs, a possible combination of both high MCL and a high degree of cross linking, and/or the effect of aluminum substitution irrespective of MCL and cross linking must be investigated further to draw solid conclusions on the relationship between the viscous behavior of C-S-H and the changes in its silicate anion structure.

The results of Young's modulus were plotted against the adsorbed dose for the control and irradiated samples and they are shown in **Fig. 3**. **Table 2** presents the results of the bootstrap statistical test for equivalence of the Young's moduli.

Six of the twelve irradiated–control pairs for Young's modulus were statistically equivalent. All three C/S irradiated–control pairs at irradiated doses of 0.145 MGy were not equivalent, and all three C/S irradiated–control pairs at irradiated doses of 0.784 MGy were equivalent, indicating that increased irradiation does not significantly affect Young's modulus. If increased irradiation at these dose levels influenced the Young's modulus, then a divergence from the control samples would be expected at higher irradiation doses, which did not occur here. However, 8 out of the 12 irradiated–control pairs showed higher mean Young's modulus for irradiated samples. It should be noted that a significant number of indents were rejected for the 0.280 MGy dose.

It is thought that the elastic modulus of C-S-H depends on factors such as water content and silicate anion structure. Other authors (Alizadeh *et al.* 2011) showed that the stiffness of C-S-H pre-conditioned to 11% RH decreases when the weight loss is less than 2% and at-

tributed that to the loss of adsorbed and interlayer water. They also observed an increase in stiffness in the interval of weight loss from 2 to 4 or 5%, followed by a decrease in stiffness when up to 12% weight was lost. They attributed the increase in stiffness to an increase in silicate polymerization and/or the formation of ionic-covalent bonds between C-S-H sheets and partially dehydrated Ca ions in the interlayer. Lattice dynamic simulations have shown that an increase in stiffness is expected in C-S-H phases with a decrease in water/Ca ratio (Manzano *et al.* 2007). The chemical structural analyses of the samples used in the current study showed no dehydration or

changes in silicate anion structure after irradiation (Tajuelo Rodriguez *et al.* 2020); therefore, it is difficult to explain or justify the observed qualitative increase in stiffness of most of the irradiated samples with respect to their controls.

It can be noted that in the results shown in **Fig. 3**, the Young's modulus showed an apparent increase with C/S ratio. According to molecular dynamics simulations (Manzano *et al.* 2009), the Young's modulus should decrease with C/S ratio. The apparent increase found for these pellets is likely due to a higher level of compaction with increasing C/S ratio and thus lower porosity. C-S-H

Fig. 2 Bootstrap mean fit and 95% confidence intervals (dotted lines) for stress relaxation curves of control and irradiated C-S-H samples for gamma doses of 0.145 (2 month dose) and 0.280 MGy (4 month dose) (left), and 0.500 (7.5 month dose) and 0.784 MGy (12 month dose) (right).

density increases slightly with C/S ratio (Richardson 2014), and since two grams of powder were used to press each pellet, the volume of used powder decreased with C/S ratio. This resulted in more compact pellets with increasing C/S ratio. In fact, it was confirmed in separate experiments (Hunnicutt 2018) that pellets pressed using the same mass of material and under the same load had lower porosity for high C/S ratio, and lower porosity should yield a higher Young's modulus. However, porosity was not directly measured in this study. The range of modulus of elasticity for all samples was 19 to 37 GPa. This range is in accordance with other nanoindentation results (Constantinides and Ulm 2004), but in that study a

bimodal distribution of the modulus of elasticity in which the lower modulus distribution (with a mean of 22 GPa) was associated with low density C-S-H, and the higher modulus distribution (with a mean of 30 GPa) was associated with high density C-S-H was claimed. The samples used in this study were fabricated in solution with identical w/s ratio, and the Young's moduli were unimodal, indicating a phase-pure and relatively uniform material. This synthesis method should yield products closer to what is considered low density C-S-H. However, high values of modulus of elasticity (> 30 GPa) that were considered characteristic of high-density C-S-H were found. This suggests that the decrease in porosity dis-

Fig. 3 Normalized force at the end of the hold period of the stress relaxation experiments for irradiated and control C-S-H samples against gamma dose (left), and mean Young's modulus for irradiated and control samples against gamma dose (right). The control samples were not exposed to any irradiation, but were otherwise subjected to the same conditions for the same duration as the dosed samples; control and dosed samples are plotted together for easier comparison. The plots are separated for C/S ratios for clarity.

Table 3 Results of bootstrap statistical test for equivalence ($\alpha = 0.05$) creep compliance curves of control and irradiated C-S-H samples. The number of indents used after reducing the sampling for equal sample size is also indicated after the equivalence.

	CSH 0.75	CSH 1	CSH 1.33
0.784 MGy dose	Equivalent/74	Equivalent/80	Not equivalent/83

cussed previously was the main cause of the increased stiffness. It should be noted that in this study C-S-H was synthesized in solution, and not as the result of cement hydration, therefore the authors claim that the mechanical properties are similar to low and high density C-S-H that is formed during cement hydration while recognizing the different route of formation.

The creep response was also investigated for the samples irradiated at the highest dose (0.784 MGy). The creep compliance for control and irradiated samples is shown in **Fig. 5**, and the results of the bootstrap test for equivalence are presented in **Table 3**. The pair for C/S = 1 shows an almost identical response for dose and control samples that also were equivalent according to the statistical test results. The control and dose pairs for C/S = 0.75 and 1.33 show differences with the control samples having a larger creep compliance than dosed samples, although only the pair with C/S = 1.33 was found to be non-equivalent.

Similar behavior of a decrease in creep with irradiation was observed by a different author (McDowall 1971), who studied in-situ creep and shrinkage under gamma irradiation by applying a load to a concrete sample and observed less creep for the irradiated specimen when compared to the control specimen. The dose reached in that study was approximately 0.8 MGy, which is similar to the dose of 0.784 MGy reported here. Other authors also found that mortars irradiated to 0.257 MGy presented a lower creep response than their control samples (Hilloulin *et al.* 2018). With the chemical analyses of the samples used in this study showing no effect to chemically bound water or silicate anion structure after irra-

diation (Tajuelo Rodriguez *et al.* 2020), it is difficult to determine the underlying cause of a possible decrease in creep. Unlike the normalized relaxation modulus, the creep compliance is directly influenced by the porosity of the pellets; there is no evidence in this study that the porosity of the pellets was altered during irradiation, but any changes in water content due to irradiation would likely influence how stress is redistributed in the microstructure under creep loading. The dependence of creep nanoindentation measurements on porosity make it difficult to compare samples without direct measurement of the porosity; in this study the irradiated and control pellets were produced in the exact same way and differences in porosity are thought to be small. However, there is still some uncertainty in the porosity of the pellets that may be obscuring changes in viscoelastic behavior with irradiation. It should be noted that the qualitative trends between irradiated-control pairs in creep compliance and Young's modulus are in general agreement; the model used to calculate creep compliance is inversely proportional to the Young's modulus, and the irradiated-control pairs for the creep compliance and Young's modulus data display this inverse relationship.

The viscoelastic behavior of the C-S-H samples as measured by stress relaxation and creep experiments is not strictly the same; the creep experiments pointed towards a qualitative decrease in viscous response with irradiation. This trend was seen in 2 out of 3 irradiated-control pairs, with only one of them being statistically non-equivalent, whereas the stress relaxation experiments were more aligned with an increase in viscous response with irradiation, as 9 out of 12 irradi-

Fig. 4 Normalized force at the end of the hold period against mean silicate chain length (MCL) for all irradiated and control C-S-H samples (left), and against degree of cross linking (Q^3) (right). The data for mean silicate chain length and degree of cross linking are taken from a previous study (Tajuelo Rodriguez *et al.* 2020).

ated-control pairs showed this trend, with 6 of them having statistically non-equivalent results. Nevertheless, the stress relaxation results did not show an obvious trend with dosage, which would be expected if irradiation was significantly impacting the viscoelastic behavior. Several differences exist in these two types of experiments: the normalized stress relaxation experiment is independent of porosity, while the creep experiment is not; the displacement-controlled stress relaxation experiment is not as well controlled as the load-controlled creep experiment; and there was substantially more stress relaxation data collected in these experiments than creep

data. These combined factors make it difficult to identify the cause of the apparent difference between stress relaxation and creep behavior.

The change in mechanical response due to irradiation of the C-S-H samples is not clear; other factors, such as the water content of the samples, appear to provide enough variability that the statistical analysis is not conclusive on the effect of irradiation on mechanical response. Literature indicates that water content of C-S-H can play a significant role in the mechanical behavior of C-S-H (Maruyama *et al.* 2014; Suwanmaneechot *et al.* 2020). In the current study, C-S-H was conditioned to 11% RH prior to compaction and irradiation, but relative humidity was not controlled after irradiation. The relative humidity of the samples was not controlled after irradiation because observations of the effects of irradiation in its entirety (including changes in water content) were desired. The thermogravimetry results presented in Part I of this study (Tajuelo Rodriguez *et al.* 2020) indicate that the average absolute value of the difference in water content between dose and control pairs is 1.00%, with the largest outlier being 2.67%; based on the results of Suwanmaneechot *et al.* (2020) this small of a difference in water content is not expected to significantly impact viscoelastic behavior in the low relative humidity range examined in this study. However, it is possible that the relative humidity of the C-S-H pellets approached equilibrium with the environment while in storage or during testing, thus the water content of the samples near the surface (where nanoindentation takes place) are possibly different from the thermogravimetry results. Additionally, the water content of samples with different C/S may be different after storage in a non-humidity controlled environment due to different porosities and rates of diffusion of the pellets. This is also a potential explanation for the observed differences in the normalized force and Young's modulus of control samples that were stored for different lengths of time (2 months, 4 months, 7.5 months, and 12 months) presented in **Figs. 2 and 3**. The effects of the possible different water content near the surface of the pellets may have provided enough noise to obscure statistically significant trends in mechanical behavior in relation to gamma irradiation.

While the stress relaxation experiments are theoretically independent of porosity, the difference in the pore network may impact the rate at which the C-S-H pellets come to equilibrium with the relative humidity of the environment; the water content of the pellets likely impacted the viscoelastic behavior of the C-S-H pellets to some extent, thus porosity may have played an indirect role on viscoelasticity via changes in water content of the samples. Additionally, higher relative humidity during storage of synthesized C-S-H has been found to decrease the local structural order of C-S-H as observed by increased peak width in ^{29}Si NMR measurements (Cong and Kirkpatrick 1995), which is an additional pathway for changes in viscoelastic behavior. Unfortunately, wa-

Fig. 5 Bootstrap mean fit for the creep compliance with 95% confidence intervals (dashed lines) for irradiated and control C-S-H samples for the dose of 0.784 MGy (12 month dose). The plots are separated for the three C/S ratios for clarity.

ter content was not measured after nanoindentation and the exact water content of the C-S-H during testing is unknown. The effect of irradiation at these doses are not sufficient to overcome the variation in viscoelastic behavior caused by possible changes in water content during storage and testing, leading the authors to conclude that gamma irradiation up to 0.784 MGy does not significantly influence viscoelastic behavior due to modification of the C-S-H nanostructure and crystallinity.

4. Conclusions

Nanoindentation tests to probe stress relaxation, and Young's modulus of C-S-H conditioned to 11% RH with C/S ratios of 0.75, 1, and 1.33 irradiated to gamma doses of 0.145, 0.280, 0.500, and 0.784 MGy showed no obvious trends in viscous or elastic response with irradiation dose. The normalized force for the stress relaxation tests was qualitatively lower for most of the irradiated samples with respect to their controls, indicating a qualitative increase in viscous response. However, only 6 irradiated-control pairs (out of the total 12) showing this trend were found to be statistically non-equivalent. The normalized force at the end of the hold period for stress relaxation presented no correlation with the MCL or the degree of crosslinking of the silicate chain. The elastic response, per Young's modulus, also showed no apparent variation with dose. For a given C/S ratio most samples showed similar stiffness. However, most irradiated-control pairs showed an increase in stiffness for irradiated samples with respect to their controls, although not always with statistical significance. The creep compliance for samples irradiated to 0.784 MGy was qualitatively lower for irradiated samples than for their respective control sample; 2 out of the 3 irradiated-control pairs showed this trend, but only one of them was found to be statistically non-equivalent.

The lack of obvious changes in mechanical properties of C-S-H after gamma irradiation presented in this paper match the observations shown in the companion publication with studies on chemical structural properties of the same samples (Tajuelo Rodriguez *et al.* 2020). The studies described in the companion publication showed no critical differences in total water content, interlayer water as per basal distance, or silicate anion structure. Certainly, removal of interlayer water would have caused a change in mechanical properties, but chemically bound water was not removed after the adsorbed doses of 0.145 to 0.784 MGy. It can be concluded that gamma irradiation doses up to 0.784 MGy did not significantly alter the mechanical properties of C-S-H. The maximum attained dose in this study was two orders of magnitude lower than that expected for the biological shield after 80 years of prolonged reactor operation. Experiments to explore the effects of doses of 25 MGy and 200 MGy on similar samples are being carried out. Given that other reported studies are aligned with a decrease in creep for gamma

irradiated cementitious materials (McDowall 1971; Hiloulin *et al.* 2018), the possible drop in viscous response of C-S-H with higher doses is still of interest. This potential decrease in creep could impact the ability of the cement paste to relax stresses caused by the volumetric expansion of aggregates with irradiation and may need to be considered in the development of predictive models for irradiation damage in concrete. The studies at higher doses will serve to inform these models that are being developed to aid the management of aging structures in LWRs.

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