The Influences of Neutron Irradiation on Aggregate Induced Degradation of Concrete

Reactor Concepts Research Development and Demonstration (RCRD&D)

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**Introduction**

Reactor cavity concrete, the primary support structure for the reactor pressure vessel (RPV), is exposed to chronic neutron/gamma radiation during normal operation. During long term operation, the interaction of neutron irradiation with the concrete’s constituents may cause premature degradation of the concrete structure, as highlighted by a review of concrete properties in nuclear power plant environments. At high fluence levels, as in biological shielding, neutron irradiation may cause amorphization of the crystalline components of concrete, i.e., mineral aggregates, and volume changes, which are typically expansive in nature. Volume expansion can generate tensile stresses within concrete which can induce microcracking and/or result in debonding of aggregate with the matrix. On the other hand, structural disordering can result in changes in the stability of the phase in aqueous environments.

This report presents the findings of investigations performed over 3 years through the collaboration of researchers from University of California, Los Angeles, Arizona State University, and Oak Ridge National Laboratory. The first part of the study addresses the effect of neutron irradiation on the durability of aggregates. Comparisons of aqueous dissolution rates, as a function of pH and temperature, were performed for aggregates that are either pristine (i.e., non-irradiated) or exposed to Ar⁺ ion irradiation at specified doses. These experimental results were coupled with molecular dynamics simulations of atomic scale changes in the crystallographic structure of the mineral and any resulting changes in physical properties (e.g., density) that result. The second section focuses on macroscopic effects of such changes in aggregate behavior in concrete degradation, primarily through changes in the concrete’s microstructure. Particularly, the effects akin to those originating from alkali-silica reaction (ASR) were evaluated. The project is structured to encompass 6 main tasks, as follows:

**Task 1:** Selection of aggregates in relation to their abundance and mineralogy, and their irradiation

**Task 2:** Molecular dynamics (MD): The effects of irradiation on the atomic disordering of aggregates

**Task 3:** The influences of irradiation on aggregate reactivity

**Task 4:** Reactive-transport simulation of expansive product formation in concrete microstructures

**Task 5:** X-FEM-based modeling of damage evolution due to irradiation-induced aggregates reactions

**Task 6:** Benchmarking, verification and validation of the simulation modules

Thus, a rigorous understanding of irradiation-assisted mineral alterations was used to develop a mechanistic degradation model for concrete exposed to neutrons, while considering aspects of: chemical reaction (dissolution and precipitation), mass and ion transport, and damage evolutions. The models developed were embedded in a multi-physics aging code for nuclear components and structures called Grizzly, which allows for benchmarking, verification, and validation against expansion data acquired on concrete undergoing alkali-silica reaction, a physically/chemically equivalent form of degradation that develops in the absence of radiation. These findings provide insight into the sensitivities of minerals to irradiation, by highlighting characteristics of concretes and power plants subject to such risks. The research will aid the nuclear power industry to anticipate and mitigate such risks in light of second license renewals.
Milestone/Task 1
Selection of aggregates in relation to abundance, mineralogy and their irradiation

1. Selection of mineral aggregates

Minerals were selected on the basis of their abundance in common technical aggregates used in concrete in the U.S. (Figure 1). These minerals include: calcite (CaCO₃) and dolomite (CaMg(CO₃)₂), which are the main constituents of carbonate rocks on the Earth’s surface; quartz (SiO₂), which is one of the most common rock-forming minerals, and is found in rocks including sandstone, quartzite, granite, and gneiss, among several others; and albite (NaAlSi₃O₈) and anorthite (CaAl₂Si₂O₈), which are the end-members of the plagioclase group of minerals typical of magmatic and metamorphic rocks. Almandine (Fe₃Al₂Si₃O₁₂) is one of the end-members in garnet group, and occurs as porphyroblast in schists. The minerals albite, anorthite, dolomite, and almandine were obtained from Ward’s Natural Science Company, whereas synthetic samples (“single crystals”) of quartz (001) and calcite (100) surfaces were sourced from MTI Corporation.

![Figure 1: An illustration of the most common aggregates used in U.S. (ASTM C125). [1]](image)

1.1 Sample preparation

The mineral samples were cut to sections with dimensions of 1 cm × 1 cm × 0.1 cm using a low speed diamond saw (IsoMetTM 1000, Buehler Inc.), and then embedded in a cold-cured inert acrylic resin (EpoxiCure Resin, PN 203430128: Buehler Inc.). One side of the epoxy resin was mechanically polished using 600, 800 and 1200 grit SiC abrasives and diamond pastes (from 6 down to ¼ micron) successively. The quartz (001) and calcite (100) samples have dimensions of 1 cm × 1 cm × 0.1 cm (l × w × h). Ion-beam irradiations were carried out at Michigan Ion Beam Laboratory (MIBL) at room temperature using an implantation energy of 400 keV with Ar⁺-ions to a total fluence of 1.0 x 10¹⁴ ions/cm². It should be noted that Ar⁺ ion irradiation was selected rather than neutron irradiation as (i) the former features more precise temperature and dose controls and (ii) both ion and neutron irradiation result in a similar end state, i.e., in terms of their effects on altering a mineral’s crystalline structure. [2,3]
2. Characterization of mineral aggregates

Natural rocks may contain traces of other phases distinct from their main mineralogical components. Macroscopic observations of natural samples of albite, anorthite, almandine and dolomite suggest that they are impure. To characterize the purity of the samples, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), x-ray diffraction (XRD), and Raman spectroscopy were employed, as described below.

2.1 Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS)

Energy dispersive X-ray spectroscopy (EDS) is an analytical technique that can be coupled with scanning electron microscopy (SEM). SEM-EDS can be used for elemental analysis and chemical characterization of different areas on a sample surface, with a resolution that is on the order of a few microns. [4] The working principle of EDS relies on the interaction between X-rays and the atoms on the sample surface. To stimulate characteristic X-rays from a specimen, high-energy electrons are focused on the sample, and the incident beam excites electrons in the inner shell of an atom, creating an electron hole that is then filled by electrons in the outer shell, releasing energy in the process. The amounts and energies of X-rays emitted from the sample are measured by a spectrometer to create a unique emission spectrum depending on the atomic structure. [5]

Prior to SEM measurements, selected mineral samples were powdered to few micrometers in size using a ball mill, and then coated with Au for 1 minute using a Hummer® 6.6 Sputter Coater, producing a film with thickness of about 6-7 nanometers. SEM imaging was carried out using secondary electrons and backscattered electrons using a FEI Nova NanoSEM 230 (7 kV, 80 pA).

2.2 X-ray Diffraction (XRD)

Selected samples were analyzed using powder X-ray diffraction (XRD) to identify the crystalline phases that are present. [6] The pristine mineral samples were ball milled to produce particles that are a few micrometers in size. XRD patterns were recorded using a Bruker D8-Advance powder X-ray diffractometer in 0-0 Bragg-Brentano geometry, using Cu Kα radiation (λ = 1.5406 Å), 40 kV accelerating voltage, and 40 mA beam intensity. A 2θ range of 10° to 70°, a 2θ scan step size of 0.02°, and an exposure time of 0.5 seconds per step were employed. The peak locations and relative peak intensities in the X-ray diffractograms provide information on the particular crystalline compounds that are present in the sample.

2.3 Raman Spectroscopy

Raman spectroscopy is a technique for measuring the vibrational and rotational molecular bonding in a system. [7] Therefore, Raman spectroscopy was applied to observe structural changes in the mineral samples after ion-implantation. Similar to SEM-EDS and XRD, Raman spectroscopy also provides a fingerprint spectrum for the species present in a sample. [8] The working principle for Raman analysis relies on both elastic (Rayleigh) and inelastic (Raman) scattering of a laser beam. A monochromatic laser of wavelength near that of visible light interacts with the changing polarizability of the molecule and excites the molecule from the ground state to a higher energy state, resulting in scattering of laser and shifts in energy above (anti-Stokes) or below (Stokes) the incident laser energy. [9] These shifts in energy reveal information on the changes in vibrational modes in the molecules. [10] Both pristine and implanted mineral samples were probed using a Renishaw inVia confocal Raman microscope with laser beam of near-infrared wavelength, 785 nm, and a wavenumber range of 0 – 2500 cm⁻¹. At least two different areas (with
diameters of 100 µm) on the surfaces were probed. The spectra were obtained by averaging three measurements at each sample area.

3. Results

3.1 Scanning Electron Microscopy–Energy Dispersive X-ray Spectroscopy

The elemental compositions (as oxides) of albite, anorthite, almandine, and dolomite from natural rocks measured by SEM-EDS are given in Table 1. Traces of Fe and K, Na and K, and Mg and Zr were detected in albite, anorthite, and almandine, respectively. In addition, a significant amount of Mg (>10% as oxide) was present in the anorthite sample, whereas a significant amount of Ca (>10% as oxide) was observed in almandine. Notably, Fe was not detected in this sample. The amounts of Mg and Ca in the dolomite sample are higher and lower respectively than the stoichiometric values for pure dolomite. The SEM-EDS imaging and elemental analyses were performed using ETD objectives, which measure secondary scattering and backscattering electrons. The selected areas were larger than 1000 µm², and the measurements were repeated at least 3 times.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Albite</th>
<th>Anorthite</th>
<th>Almandine</th>
<th>Dolomite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mass %</td>
<td>mass %</td>
<td>mass %</td>
<td>mass %</td>
</tr>
<tr>
<td>SiO₂</td>
<td>73.62 ± 0.89</td>
<td>67.92 ± 0.60</td>
<td>55.45 ± 4.30</td>
<td>-</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>14.70 ± 0.57</td>
<td>8.58 ± 0.43</td>
<td>31.14 ± 2.36</td>
<td>-</td>
</tr>
<tr>
<td>Na₂O</td>
<td>8.77 ± 0.47</td>
<td>1.10 ± 0.12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.88 ± 2.97</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.03 ± 0.22</td>
<td>0.82 ± 0.12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CaO</td>
<td>-</td>
<td>9.88 ± 0.40</td>
<td>10.77 ± 2.92</td>
<td>11.10 ± 1.12</td>
</tr>
<tr>
<td>MgO</td>
<td>-</td>
<td>11.71 ± 0.29</td>
<td>0.67 ± 0.35</td>
<td>41.47 ± 8.99</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>-</td>
<td>-</td>
<td>1.97 ± 0.28</td>
<td>-</td>
</tr>
<tr>
<td>CO₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>47.43 ± 3.37</td>
</tr>
</tbody>
</table>
3.2 X-ray Diffraction

The XRD patterns of the albite, almandine, and dolomite samples are qualitatively similar to those reported in the literature [11,12] and the International Centre for Diffraction Data (ICDD) reference codes listed in Table 2. However, the diffractogram for anorthite is more complex (Figure 3b). A mineral is defined as anorthite if the anorthite content (An%) is > 90%. We determined from an XRD database (Reference code: 01-089-1480) that our 'anorthite natural rock sample' has an An% ~70%, corresponding to labradorite (An%: 50%-70%) or bytownite (An%: 70%-90%). From comparisons with SEM-EDS data, the additional peaks in the XRD pattern of anorthite (e.g., see unlabeled peaks in Figure 3b) were inferred to correspond with the hydrated calcium magnesium silicate phases (e.g., magnesiosadanagaite, actinolite, tremolite, etc.) [13].

The broad background in the XRD pattern of almandine (e.g., see Figure 3c) suggests the presence of amorphous phases in the sample; the additional peaks were inferred to signify hydrated calcium silicate phases. [13]

| Table 2: X-ray diffraction reference codes used in comparison with the samples, as shown in Figure 3. |
|---------------------------------|---------------------------------|---------------------------------|
| Reference code                  | Minerals                        |
| Albite (NaAlSi3O8)              | 01-075-1142                     | Na(AlSi3O8)                     |
| Anorthite (CaAl2Si2O8)          | 01-089-1480                     | Ca0.78Na0.22Al1.78Si2.22O8      |
| Almandine (Fe3Al2Si3O12)        | 01-081-0541                     | Mg0.6Fe2.4Al2Si3O12             |
| Dolomite (CaMg(CO3)2)           | 00-001-0942                     | CaMg(CO3)2                     |
3.3 Raman Spectroscopy

Raman spectroscopy was employed on both pristine and implanted mineral samples to investigate the change in bonding structure before and after irradiation. For instance, the degree of Al/Si ordering can be measured using FTIR and Raman analysis. [14] The main difference between these two techniques lies in the nature of molecular bonding that is investigated. [15] Raman spectroscopy can be used to measure the change in the polarizability of the molecular bond during vibration, whereas FTIR enables measurement of the change in dipole moment during vibrations. [14] In Raman and FTIR spectroscopy, an increase in the degree of Al/Si ordering is manifested by an increase in density, number, sharpness, and locations of peaks.

The degree of structure disorder can be derived from two parameters, namely: (1) the number of peaks in a certain range of wavenumber, and (2) the displacement of the peak position relative to a reference. [16] For example, as the structure becomes more disordered, the number of peaks would decrease and peak positions would shift towards lower wavelength, in general.
The Raman spectra for albite, anorthite, almandine and dolomite minerals are shown in Figures 4. Measurements at different spots on the surface are represented by different colors. The red and orange lines in each figure represent the spectra for the samples that have been implanted, whereas the blue and green lines correspond to pristine samples. Qualitative differences in the pristine and implanted samples are encircled in Figure 4a. The irradiated silicate minerals (albite, anorthite, and almandine) have characteristic peaks that are slightly shifted in position or have reduced intensities in comparison to their pristine counterparts. In some cases, there are fewer peaks on implanted samples. In contrast, the spectra for the pristine and implanted carbonate mineral dolomite are qualitatively similar, and reductions in the intensities of the peaks were not evident. This suggests that dolomite did not undergo substantial structural disorder after implantation, as supported by previous observations. [17] The broad peak at high wavenumbers (~1500 cm\(^{-1}\)) likely corresponds to the fluorescence background. The background fluorescence could potentially be reduced by performing measurements using a higher incident wavelength, as shown previously. [18]

![Figure 4: The Raman spectra of pristine and implanted (a) albite, (b) anorthite, (c) almandine, and (d) dolomite. Spectra in blue and green, and red and orange represent two different spots on the same pristine and implanted samples, respectively. Qualitative differences in spectra are marked by dark blue circles in (a), (b), and (c).](image-url)
Milestone/Task 2
Molecular dynamics (MD): The effects of irradiation on atomic disordering

1. Objective
This task worked towards two objectives: (a) to quantify the disordering and swelling induced by irradiation on aggregate minerals and (b) to assess the effect of amorphization on the topology of the atomic network, to ultimately predict the variations of reactivity of each mineral.

2. Simulations of irradiation-induced damage
Molecular dynamics (MD) simulations of irradiation damage were carried out on the following aggregate minerals: albite, almandine, anorthite, calcite, dolomite, diopside (MgCaSi$_2$O$_6$), enstatite (MgSiO$_3$), and quartz. These minerals were chosen based on their abundance as concrete aggregates. Note that, in addition to the minerals chosen in [T 1], a few other minerals were included for the MD simulations: diopside, and enstatite.

2.1 Simulation methodology
Realistic MD simulations of irradiation-induced damage in minerals were carried out in the open-source LAMMPS [19] package, following a well-established methodology. [20] First, a randomly chosen atom is accelerated with a kinetic energy equivalent to that of the targeted incident neutron, 600 eV in the present case. Weighted probabilities based on the neutron cross-sections of the respective elements (see Table 3) are considered when choosing the incident atom. The accelerated atom then collides with other atoms, thereby resulting in a ballistic cascade. Subsequently, a spherical region is created around the impacted zone, outside which atoms are kept at a constant temperature of 300 K by a Berendsen thermostat. [21] In contrast, the dynamics of the atoms inside the sphere is treated in the NVE ensemble to avoid any spurious effects of thermostat. A variable timestep is used during the ballistic cascade to avoid potential numerical errors associated with excessive collisions and overlapping of atoms; a timestep of 0.5 fs is used otherwise. The dynamics of the cascade is simulated for 15 ps, which was found to be sufficiently long to ensure the convergence of both temperature and energy. Finally, after each collision, the system is further relaxed in the NPT ensemble at 300 K and zero pressure for another 5 ps. This enables the system to adjust its density upon irradiation. This process is then repeated in an iterative fashion, with different knock-on atoms, until the system exhibits saturation in both enthalpy and density. Note that the damage produced by such sequential irradiation is essentially similar to that of simultaneous particle irradiation, [22] such that the generality of the results is maintained.

Due to the large region that is affected during each ballistic cascade, large system sizes are required to avoid potential spurious self-interactions arising from the periodic boundary conditions. Herein, the system size was determined by repeatedly knocking each atom of the primitive cell, with the target radiation energy and in random directions. The study was conducted on all the different species of atoms present in the system. The maximum distances travelled by each of the impacted atoms were then recorded. Eventually, the size of the system was chosen to be at least twice as large as the maximum distance among all the recorded ones. It is worth noting that, to offer realistic results, MD simulations require the use of accurate inter-atomic potentials. In particular, in the case of irradiation simulations, the inter-atomic potential must correctly describe both the pristine and disordered structures of the relevant system with a fixed set of parameters. Although using a single “universal” potential would constitute an ideal option, such a potential is presently unavailable. Rather, each potential is specifically parametrized to optimally predict the
properties of a family of materials. As such, for each family of aggregates, we selected the best available potential based on its ability to predict a realistic density, structure, and elastic tensor, both for the pristine mineral and its glassy counterpart. For quartz, we used the ReaxFF potential, with parameters taken from Manzano et al. [23] For other silicate minerals, a Buckingham potential parametrized by Teter was used, splined with ZBL potential to ensure realistic short-range repulsive interactions during the ballistic cascades (Table 4). [24] The carbonate minerals (calcite and dolomite) were simulated using the potentials from Raiteri et al., [25] which were parameterized specifically for dolomite and calcite and which can simulate both the ordered and disordered phases.

### Table 3: Neutron cross-sections of the elements found in the considered aggregate minerals.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Element Name</th>
<th>Neutron cross-section (barns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aluminum (Al)</td>
<td>1.35</td>
</tr>
<tr>
<td>2</td>
<td>Silicon (Si)</td>
<td>2.00</td>
</tr>
<tr>
<td>3</td>
<td>Sodium (Na)</td>
<td>3.15</td>
</tr>
<tr>
<td>4</td>
<td>Oxygen (O)</td>
<td>3.83</td>
</tr>
<tr>
<td>5</td>
<td>Calcium (Ca)</td>
<td>2.55</td>
</tr>
<tr>
<td>6</td>
<td>Magnesium (Mg)</td>
<td>3.91</td>
</tr>
<tr>
<td>7</td>
<td>Iron (Fe)</td>
<td>9.97</td>
</tr>
</tbody>
</table>

### Table 4: Teter potential parameters for X–O interactions, where X= Si, Ca, Al, Mg, Na, Fe, O.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Element</th>
<th>Charge</th>
<th>A (eV)</th>
<th>( \rho ) (Å)</th>
<th>C (eV/Å⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Si</td>
<td>2.40</td>
<td>13702.910</td>
<td>0.194</td>
<td>54.681</td>
</tr>
<tr>
<td>2</td>
<td>Ca</td>
<td>1.20</td>
<td>7747.183</td>
<td>0.253</td>
<td>93.109</td>
</tr>
<tr>
<td>3</td>
<td>Al</td>
<td>1.80</td>
<td>12201.420</td>
<td>0.196</td>
<td>31.997</td>
</tr>
<tr>
<td>4</td>
<td>Mg</td>
<td>1.20</td>
<td>7063.491</td>
<td>0.211</td>
<td>19.210</td>
</tr>
<tr>
<td>5</td>
<td>Na</td>
<td>0.60</td>
<td>4383.756</td>
<td>0.244</td>
<td>30.700</td>
</tr>
<tr>
<td>6</td>
<td>Fe</td>
<td>1.20</td>
<td>19952.000</td>
<td>0.183</td>
<td>4.658</td>
</tr>
<tr>
<td>7</td>
<td>O</td>
<td>-1.20</td>
<td>2029.220</td>
<td>0.344</td>
<td>192.580</td>
</tr>
</tbody>
</table>

3. Results
3.1 Albite (NaAlSi₃O₈)

Albite is a tectosilicate mineral belonging to the tectosilicate feldspar family, which consists of Al and Si tetrahedra in the molar ratio of 1:3. Na⁺ act as charge-balancing cations, leaving all O atoms in the structure as bridging oxygen (BO). The Si–O–Al and Si–O–Si bond angles are distributed in the ratio of 1:1. The evolution of density upon irradiation is plotted in Figure 5a. During irradiation, albite exhibits a reduction in density from 2.61 g/cm³ to 2.44 g/cm³. Further, an investigation of the final irradiated structure of albite reveals a broadening in the distribution of the Si–O–Si bond angles. In contrast, the coordination numbers of Si and Al are not significantly affected by irradiation. Hence, the overall increase of the volume primarily arises from the expansion of the silicate network, due to irradiation-induced disordering.

3.2 Anorthite (CaAl₂Si₂O₈)
Anorthite is the calcium-rich end-member of the feldspar family, which like albite is characterized by a framework silicate network. Since the amount of Al and Si atoms present in the mineral are equal, anorthite has alternate Al and Si tetrahedra connected by BO atoms to form a 3-D packed structure. Interestingly, anorthite exhibits a slight increase in density upon irradiation, as shown in Figure 5b. This increase is not linked to any significant change in the short-range order (e.g., coordination number or bond length). However, as opposed to the pristine structure, we note the appearance of Si–O–Si and Al–O–Al bond angles upon irradiation, which results in a more compact structure.

![Figure 5: Evolution of the density of (a) albite and (b) anorthite under irradiation.](image)

3.3 Almandine (Fe₃Al₂Si₃O₁₂)
Almandine is a nesosilicate which consists of isolated SiO₄⁴⁻ tetrahedra connected by cations. Aluminum is present with an octahedral environment, i.e., connected to six O atoms. During irradiation, almandine exhibits a reduction of density, from 4.2 g/cm³ to 3.4 g/cm³, as shown in Figure 6a. An analysis of the final structure revealed that all of the Al atoms underwent a transition from octahedral to tetrahedral coordination environments upon irradiation, which induces the observed expansion – since the tetrahedral structure features a lower packing fraction than the octahedral structure.

3.4 Quartz (SiO₂)
Quartz, one of the most abundant minerals in Earth’s crust, belongs to the tectosilicate family. It has a trigonal crystal structure with each O forming a bridge between two Si atoms. Under irradiation, quartz exhibits significant swelling, as shown in Figure 6b. Interestingly, the final density of irradiated quartz is close to that of glassy silica (2.2 g/cm³). An investigation on the final irradiated structure revealed that the distribution of Si–O–Si bond angles is significantly broader, which primarily explains the observed swelling.
3.5 Calcite (CaCO₃)

Calcite belongs to the carbonate family of minerals, with an ionic bond between Ca atoms and CO₃ groups. As shown in Figure 7a, calcite does not exhibit any notable change in density. This can be attributed to the non-directional nature of the ionic bonds, which, as such, can easily reorganize after irradiation. Although the final structure exhibits a slightly disordered nature as compared to that of the pristine calcite, we observe that the mineral remains largely unaffected by irradiation.

3.6 Dolomite (CaMg(CO₃)₂)

Dolomite, which belongs to the carbonate family, has a structure similar to calcite with alternate Ca atoms being replaced by Mg. The density of pristine dolomite is higher than that of calcite. Under irradiation we observed that similar to calcite, dolomite does not exhibit any notable changes in density (from 2.895 g/cm³ to 2.863 g/cm³), as shown in Figure 7b.

3.7 Diopside (MgCaSi₂O₆)

Diopside is a single-chain inosilicate belonging to the pyroxene family. Tetrahedral SiO₄⁴⁻ groups are connected to form a chain-like structure, with Mg and Ca placed alternately. The irradiated mineral exhibits a 10.9% decrease of density, as shown in Figure 8a. These results are
consistent with those for albite and quartz, wherein the loss of long-range order of the silicate network causes an overall expansion of the phase.

3.8 Enstatite (MgSiO₃)

Enstatite is an inosilicate with a structure similar to diopside. The Ca atoms present in diopside are completely replaced by Mg in enstatite. As expected from their structural similarity, enstatite and diopside exhibit similar propensities for swelling under irradiation. Enstatite shows an 8.6% decrease in density after complete amorphization, as shown in Figure 8b.

![Figure 8: Evolution of the density of (a) diopside and (b) enstatite under irradiation.](image)

4. Predicting the effect of irradiation on reactivity

We now assess the effect of irradiation on the atomic topology, which serves as an input for a model which enables predictions in changes in dissolution rate within the framework of topological constraint theory (TCT).

4.1 Topological constraint theory

TCT reduces complex atomic networks into simple trusses of nodes (atoms) connected by mechanical constraints (chemical bonds). As such, TCT captures the important atomic topology, while filtering out less relevant details that ultimately do not affect macroscopic properties. [26] Specifically, the rigidity of a network is assessed by determining the number of topological constraints per atom, \(n_c\). In atomic networks, the constraints comprise the radial bond-stretching (BS) and angular bond-bending (BB) chemical atomic bonds, which maintain the bond lengths and angles fixed around their average values, respectively. As per Maxwell's stability criterion, [27] atomic networks can then be described as (1) flexible \((n_c < 3)\), showing floppy internal modes of deformation, (2) stressed-rigid \((n_c > 3)\), featuring eigenstress due to mutually incompatible constraints, or (3) isostatic \((n_c = 3)\), being rigid but free of eigenstress. Note that, here, the value “three” corresponds to the number of degrees of freedom per atom in a three-dimensional network.

Elucidating the effect of irradiation on the rigidity of the atomic network requires the enumeration of the number of constraints acting between the atoms. For fully a connected homogeneous network, e.g., as in Ge–Se glasses, the constraints enumeration is straightforward and depends only on the coordination number (CN), \(r_i\), of each species. Thus, each atom features \(r_i/2\) BS constraints, each constraint being shared by two atoms, and \(2r_i - 3\) BB constraints, which
corresponds to the number of independent angles required to define a polyhedron. Therefore, the total number of constraints per atom $n_c$ is given by:

$$n_c = \frac{<r>}{2} + 2 <r> - 3$$

where $<r>$ is the average coordination number of the atoms. In contrast, enumerating constraints in an irradiated mineral is complicated by the following difficulties: (1) A given species can feature various coordination numbers due to the formation of defects, [20] resulting in varying number of constraints for the same species, (2) the angular BB constraints, e.g., Si–O–Si bonds in quartz, are associated with lower energies than radial BS constraints, and, as such, can become broken upon irradiation. To tackle these issues, we enumerated the number of constraints by relying on MD simulations. This method is based on an inverse approach, wherein the trajectory of an atom is used to deduce the number of underlying constraints constraining its motion. The basic idea of this method is that an active constraint would maintain bond lengths or angles fixed around their average values, whereas a broken or missing constraint would allow large atomic motion. Hence, to obtain the number of BS and BB constraints acting on a given atom, we estimate the radial and angular excursions of each of its neighbors, respectively.

5. Results

5.1 Quartz

The constraints enumeration is first detailed for the case of quartz. The radial excursion of each neighbor was evaluated by computing the partial pair distribution functions (PDFs) of O and Si atoms, as well as the contributions of each neighbor 1, 2, ..., 6, where neighbors are ranked with respect to their distances from the central atom. Note that, here, the choice of the value 6 is arbitrary, although it must be large enough to ensure that it encompasses all potential constraints formed around a given atom. The radial excursions of the neighbors are then estimated from the second moments of these distributions. Such radial excursions, as computed in quartz, are plotted as a function of neighbor number $N$ in Figure 9a. We observe a clear shift from low to high radial excursions, which correspond to intact and broken BS constraints, respectively. As expected, the number of intact BS constraints corresponds here to the coordination of each species, i.e., 4 and 2 for Si and O, respectively. In a similar fashion, the angular excursion of each neighbor is evaluated by computing the partial bond angle distribution of each triplet of atoms $(i, 0, j)$, where 0 denotes the central atom considered, and $(i, j)$ all the 15 possible pairs formed among the 6 nearest neighbors. The angular excursion is then assessed by calculating the second moments of these distributions. Once again, as shown in Figure 9b, we observe a clear jump between low and high angular excursions, which represent intact and broken BB constraints, respectively. Here, we find 1 and 5 intact BB constraints per O and Si, which fixed the inter- and intra-tetrahedral angles, respectively. Altogether, this method provides a robust and non-arbitrary enumeration of the number of constraints in quartz.
Figure 9: (a) Radial excursions of each neighboring atom with respect to central Si and O atoms. Note that intact and broken BS constraints are associated with significantly different (low and high, respectively) radial excursions. (b) Angular excursions around central Si and O atoms. Note that, as in the case of BS constraints, the angular excursions associated with intact and broken BB constraints significantly differ.

This methodology can be used to track the irradiation-induced variation in $n_c$, as shown in Figure 10. First, we observe that, upon irradiation, $n_c$ decreases towards $n_c = 3$, which is the value expected for glassy silica, as the high glass transition temperature induces the breakage of the Si–O–Si BB constraints. Second, $n_c$ is noted to cross the value of three at about $1.2 \times 10^{21}$ keV/cm$^3$ deposited energy, which effectively separates a stress-rigid from a flexible domain. As shown in the inset in Figure 10, this transition arises primarily from the decrease in the number of angular BB constraints upon irradiation, which results from the breakage of Si–O–Si bonds, as well as a small fraction of O–Si–O BB constraints. This suggests that irradiation preferentially affects these weaker angular constraints, while it has little, if any, effect on the stronger radial Si–O BS constraints. Note that the trend in the evolution of $n_c$ follows a similar trend as that of the density upon irradiation. Since $n_c$ controls the reactivity of minerals, these results suggest that fully irradiated quartz features a dissolution rate fairly similar to that of glassy silica.

5.2 Other minerals

Similar constraints enumerations were carried out for the other minerals considered herein. Overall, we observe that, in most cases, the radial BS constraints are unaffected by irradiation, except in the case of almandine, wherein the coordination number of Al atoms is reduced from 6 to 4, thereby reducing the number of active BS constraints. In silicate systems, Si–O–Si bond-bending constraints are found to become consistently broken upon irradiation, as in the case of quartz. In contrast, in carbonate minerals, all constraints (BS and BB) are found to remain intact, so that no variations in $n_c$ are observed. The calculated change in $n_c$ ($\Delta n_c$) for all considered minerals are shown in Table 5. Interestingly, as shown in Figure 11a, we observe a linear correlation between $\Delta n_c$ and the relative variation of density upon irradiation. Note that the constraints that are broken upon irradiation ($\Delta n_c$) correspond to the “weaker constraints” of the networks, that is, those associated to a lower energy. This demonstrates that the number of weak constraints per atom, $\Delta n_c$, can be used as metric to predict the extent of irradiation-induced swelling.
Figure 10: The evolution of the number of constraints per atom, \( n_c \), in irradiated quartz as a function of the deposited radiation energy. The data are fitted by an exponential function. The dashed red line indicates the position of the rigidity transition \( (n_c = 3) \), which effectively separates the stressed-rigid from the flexible domain (shaded region). The inset shows the repartition of radial BS and angular BB constraints.

Table 5: Variation of the number of constraints per atom upon irradiation \( (\Delta n_c) \).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Weak constraints per atom ( (\Delta n_c) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albite</td>
<td>-0.307</td>
</tr>
<tr>
<td>Anorthite</td>
<td>0.113</td>
</tr>
<tr>
<td>Almandine</td>
<td>-0.650</td>
</tr>
<tr>
<td>Quartz</td>
<td>-0.617</td>
</tr>
<tr>
<td>Calcite</td>
<td>0</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0</td>
</tr>
<tr>
<td>Diopside</td>
<td>-0.388</td>
</tr>
<tr>
<td>Enstatite</td>
<td>-0.272</td>
</tr>
</tbody>
</table>

Figure 11: Percentage change in structural density of each mineral upon irradiation with respect to the corresponding weak constraints per atom.
Milestone/Task 3a
The influences of ion (Ar\(^+\), H\(^+\)) irradiation on aggregate reactivity

1. Objective
This milestone aims to correlate atomic scale alteration and amorphization of the structures of select aggregates (quartz, calcite, dolomite, albite, anorthite, and almandine) before and after Ar\(^+\) irradiation to the measured changes in their chemical reactivity (dissolution rate) in high pH solvents at room temperature.

2. Materials and methods
2.1. Sample preparation
The mineral samples were sectioned into the dimension of 1 cm × 1 cm × 0.1 cm using a low speed diamond saw (IsoMet\(^{\text{TM}}\) 1000, Buehler Inc.) and then embedded in a cold-cured, inert, acrylic resin (EpoxiCure Resin, PN 203430128: Buehler Inc.). The embedded samples were polished successively using 600, 800, and 1200 grit SiC abrasives and diamond pastes (from 6, 3, 1 to 0.25 µm), and then fixed on a Thorlabs Inc. kinematic mount to facilitate handling during the dissolution experiments.

Ar\(^+\)-irradiated samples were prepared at Michigan Ion Beam Laboratory (MIBL), [28] where ion-beam irradiations were carried out at room temperature using an implantation energy of 400 keV with Ar\(^+\) ions to a total fluence of 1.0 x 10\(^{14}\) ions/cm\(^2\). While the implanted samples were mounted on a resin as mentioned above, no mechanical polishing of their surfaces after irradiation was carried out so as to maintain the integrity of the disordered near-surface layer that forms following Ar\(^+\) irradiation.

The solutions used include: deionized (DI) (>18.2 MΩ•cm) water (pH 6.8), 0.1 mM NaOH (pH 10), 10 mM NaOH (pH 12), and 100 mM NaOH (pH 13). The high pH levels were selected to simulate conditions prevalent in ordinary portland cement (OPC) concrete environments, which hosts a mature state pH ≥ 12.5. [29,30] The NaOH pellets used were of ACS reagent grade. The pH of the solutions was measured using a ThermoFisher Scientific Orion Versa Star Pro pH Benchtop Multiparameter Meter calibrated over the range 2 ≤ pH ≤ 13 at the relevant measurement temperature.

2.2. Vertical scanning interferometry
To relate irradiation-induced atomic-scale alterations to the mineral’s chemical durability, the dissolution rates of pristine and ion-implanted samples were measured using vertical scanning interferometry (VSI) at room temperature (25 ± 1°C). This technique enables the measurement of surface topographies (i.e., three-dimensional images) with nanoscale resolution (on the order of 1-2 nm in the vertical direction) over large imaging areas (on the order of 10s of mm\(^2\)). Herein, a 50× Mirau objective was used (numerical aperture, N.A. = 0.55), which gives a lateral resolution of 163 nm. With this set up, a single image encompasses a field of view (FoV) of 170 µm × 170 µm. For a stitched image grid consisting of A × B (where A = 10 and B = 3) images, the cumulative field of view is on the order of 1240 µm × 440 µm. Importantly, by directly tracking the surface retreat (i.e., change in height vis-à-vis an unchanging reference) following immersion in a solution as a function of time, VSI can be used to precisely measure the dissolution rate of a solid, while being indifferent to the fate of dissolved species and the stoichiometry therein (e.g., due to incongruency in dissolution). [31,32]

A “reference area” on a planar mineral sample was covered with an inert silicone mask.
prior to submerging in a solution over a period of time using a liquid-to-solid ratio (l/s, mass basis) of ~500. As a result, the masked area remains unaffected upon contact with the solution while the unmasked area dissolves, i.e., it shows a reduction (retreat) in height over time. Before contact with the solution (“time-zero” image) and after predefined solution contact times, the sample surface was imaged using VSI. Special care was taken to (i) evacuate any residual solution from the albite surface by exposure to a brief stream of compressed N₂ prior to imaging and (ii) minimize contact of the immersion solution with CO₂ in air, which could alter its pH due to carbonation.

The VSI images thus acquired after nulling the surfaces were analyzed in Gwyddion (ver. 2.47) [34] to assess the change in height of the dissolving surface with respect to the unchanging reference area as a function of time. The change in height, \( h \), as a function of time, \( t \), \( \frac{\Delta h}{\Delta t} \), nm/h when normalized by the molar volume of the mineral yields its molar dissolution rate (mol/m²/s). Dissolution rates determined in this manner are expected to have a maximum uncertainty of up to 10% due to the various sources of variability inherent in VSI measurements, e.g., low-frequency vibrations that may not be fully damped by the vibration isolation system or temperature fluctuations in the environment.

### 2.3 Fourier-transform infrared spectroscopy (FTIR)

FTIR studies were performed on the pristine and irradiated samples using an Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (ATR-FTIR, PerkinElmer Spectrum Two) at room temperature. Polished surfaces were pressed by ~90 N onto a diamond/ZnSe composite crystal to ensure good contact and generate total internal reflection. The spectra from an average of 4 scans over the wavenumber range of 2000–400 cm\(^{-1}\) with spectral resolution of 1 cm\(^{-1}\) are reported herein.

### 2.4 Raman spectroscopy

The peaks observed in a Raman spectrum arise from specific molecular vibrations or rotations. Both pristine and implanted samples were probed using a Renishaw inVia confocal Raman microscope with diode laser beam of near-infrared wavelength of 785 nm. The spectra were obtained at 1 cm\(^{-1}\) resolution for a 10 s exposure of the CCD detector in the wavenumber region 0–2500 cm\(^{-1}\). Three spectra at 2 different areas on the surface each having a spot diameter of 100 µm were collected.

### 2.5 Zeta potential measurement

The zeta potential of finely powdered particulates (d\(_{50} \approx 20 \mu m\)) was measured by suspending 1 g of particulates in 100 mL Milli-Q deionized water (>18 MΩ•cm), and then 0.5 mL of the suspensions was added to the appropriate pH solvents (pH 1, 2, 4, 6, 10, 12 and 13) using NaOH or HCl. The test suspensions were sonicated for 1 minute after which 1.5 mL of the suspension containing the particulates was transferred into a cuvette for zeta potential measurements. Zeta potentials were measured using a ZetaPALS analyzer (Brookhaven Instruments Corporation) that used an acoustic electrophoresis (i.e., streaming potential) approach. At each pH, ten discrete measurements of zeta potential were obtained and were then averaged to obtain statistically representative data.
2.6 Topological constraint theory

As described above, TCT captures the important atomic topology while filtering out less relevant details that ultimately do not affect macroscopic properties. [26] The TCT approach allows us to characterize the reactivity of minerals by a simple metric ($n_c$) and, as such, offers a convenient framework to assess the effect of irradiation on reactivity. Indeed, previous studies has revealed that the dissolution rate of crystals and glasses depends on $n_c$, following an Arrhenius-like relationship: [35]

$$K = K_0 \exp \left( \frac{-n_c E_0}{RT} \right)$$

where $K$ is the dissolution rate, $K_0$ is a rate constant that depends on the chemistry of the solution, and $E_0$ is the energy required to break a unit constraint per atom. Note that the dissolution rate decreases as $n_c$ increases, which is in agreement with the idea that a material featuring low-energy internal mode of deformation (floppy modes) dissolves faster than a more rigid system.

3. Results
3.1 Carbonate minerals
3.1.1 Dissolution rates

The dissolution rates of pristine and implanted natural carbonate minerals were measured over a relatively short period of time (~8 hours) considering their higher dissolution rates as compared to silicate minerals. Figure 12 shows the measured dissolution rates of the irradiated and non-irradiated carbonate minerals.

3.1.1.1 Calcite (CaCO$_3$)

To compare the dissolution rates of calcite, the previously reported data collected from Plummer et al. (1978), Busenberg et al. (1986), Chou et al. (1989), Shiraki et al. (2000) and Dolgaleva et al. (2005) are also plotted. [36-40] For most of the carbonate minerals, dissolution rate remains constant over pH ~6–10, and starts to decrease with solvent pH at the highly alkaline regime (pH > 10). Our measured pristine and irradiated calcite dissolution rates are within the range of calcite dissolution rates reported in the literatures. Although all the published data selected were obtained under similar experimental environments, i.e. solution flow, solvent pH, and temperature, a variation in calcite dissolution rates by around one order of magnitude is evident. The dissolution rates for irradiated calcite at pH between 10 and 13 are also shown in Figure 12; these rates are within the range of rates observed for calcite. Hence, it is clear that irradiation does not result in significant changes in the carbonates’ reactivities.
3.1.1.2 Dolomite (CaMg(CO$_3$)$_2$)

The behavior of dolomite following irradiation is fairly similar to calcite as shown in Figure 12. Specifically, the dissolution rates of dolomite before and after irradiation are indistinguishable from each other and are consistent with previously reported values (see Figure 12). It is noted that the slight decrease, if any, in the dissolution rates of implanted carbonate minerals results from the distortion of the carbonate groups. [41] Our measured dissolution rates agree with previously reported values obtained at the same pH conditions by Chou et al., [36] which are on the order of $10^{-11}$ mol/cm$^2$/s. The small difference in dissolution rates can be traced to different origins of the dolomite (of a natural origin) and the presence of impurities. Moreover, in agreement with the data from the literature, [36] dolomite is noted to have a lower dissolution rate than calcite. This is on the account of dolomite being a carbonate which consists of Ca and Mg. Since Ca is released more rapidly than Mg, the dolomite surface becomes MgCO$_3$-enriched, as illustrated in the two-step chemical reaction given below:

\[
\text{CaMg(CO}_3\text{)}_2 + \text{H}^+ \rightarrow \text{MgCO}_3 + \text{Ca}^{2+} + \text{HCO}_3^- \tag{3}
\]

\[
\text{MgCO}_3 + \text{H}^+ \rightarrow \text{Mg}^{2+} + \text{HCO}_3^- \tag{4}
\]

Here, while the first step is rapid, the second is slower and, hence, rate-controlling. [36]

3.1.2 Atomic structure alteration: TEM, FTIR, Raman

Radiation damage in minerals generally originates from alterations of their atomic crystal structure. In particular, an accumulation of disordering can lead to substantial structural changes, such as a complete loss of crystallinity, i.e., amorphization. To evaluate the structural alteration induced by irradiation, cross-sectional transmission electron microscopy (TEM), selected area electron diffraction (SAED) patterns, FTIR and Raman were acquired. [17] No changes in crystallinity are noticed in calcite after irradiation—SAED patterns of implanted and pristine regions (Figure 13) are similar and both exhibit sharp diffraction maxima.
Figure 13: Cross-sectional transmission electron microscopy (TEM) images and corresponding selected area electron diffraction (SAED) patterns from the ion implanted regions (III) and past ion end-of-range (IV) for calcite single crystal shows the lack of amorphization in calcite.

Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy were used to evaluate the occurrence of disordering. The FTIR spectra of carbonate minerals reveal major peaks at 1435–1450 cm⁻¹, 876–881 cm⁻¹ 712–730 cm⁻¹ as well as minor peaks at 2530–2550 cm⁻¹ and 1812–1818 cm⁻¹, as shown in Figure 14. These peaks have been found to correspond to various stretching and bending modes of the CO₃²⁻ groups (see Figure 15). [41-43] A comparison of the FTIR spectra for the irradiated carbonates reveal that these are generally indistinguishable from those obtained for the pristine samples.

Figure 14: Representative FTIR spectra of the pristine and irradiated (a) calcite and (b) dolomite in the 400–2000 cm⁻¹ wavenumber region.
Similarly, the Raman spectra obtained for calcite and dolomite before and after irradiation given in Figure 16 indicate that the positions and intensities of the 6 major peaks which characterize the chemical bonding on the carbonates’ surfaces remain unchanged (Table 6). These observations suggest that the pristine and the irradiated carbonates share the same nature of chemical bonding particularly as characterized by the vibrational spectra, i.e., CO$_3^{2-}$ stretching, rotation, translation, or bending. In summary, the results obtained from both Raman and FTIR spectroscopy are consistent with the limited irradiation-induced structural damage in carbonates, as also demonstrated previously by Pignatelli et al. using cross-sectional TEM and selected area electron diffraction (SAED) on calcite (Figure 13). [17]

This is further supported by our MD simulations results, which show that carbonate minerals are substantially more resistant to radiation than silicate systems (as shown in [T2]). Moreover, the calculated values of the number of constraints ($n_c$) for pristine and irradiated calcite using TCT are equal, suggesting a corresponding minor change in the dissolution rates following irradiation. As in calcite, the $n_c$ of dolomite remains the same after irradiation, which is consistent with the fact that the dissolution rates remain largely unaffected by irradiation. The change in $n_c$ for the minerals investigated—and the resulting dissolution behavior—are given in Table 9.

**Table 6:** Relevant Raman peak positions and their corresponding vibration modes for calcite and dolomite. ($\nu_i$ denotes the various modes of vibration, where $i = 1, 2, 3, 4$)

<table>
<thead>
<tr>
<th>Calcite peaks (cm$^{-1}$)</th>
<th>Dolomite peaks (cm$^{-1}$)</th>
<th>Vibrational mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>154</td>
<td>179</td>
<td>External CO$_3^{2-}$ translational modes [44]</td>
</tr>
<tr>
<td>280</td>
<td>304</td>
<td>External CO$_3^{2-}$ rotational modes [44]</td>
</tr>
<tr>
<td>710</td>
<td>725</td>
<td>Symmetric CO$_3^{2-}$ deformation ($\nu_4$) [45]</td>
</tr>
<tr>
<td>1085</td>
<td>1100</td>
<td>Symmetric CO$_3^{2-}$ stretching ($\nu_1$) [44]</td>
</tr>
<tr>
<td>1434</td>
<td>1445</td>
<td>Antisymmetric CO$_3^{2-}$ stretching ($\nu_3$) [45]</td>
</tr>
<tr>
<td>1747</td>
<td>1765</td>
<td>Out-of-plane CO$_3^{2-}$ ions bending ($\nu_2$) [44]</td>
</tr>
</tbody>
</table>
3.2. Silicate minerals

3.2.1 Dissolution rates

Silicates dissolved much slower than carbonates, as expected. Specifically, albite, anorthite, almandine and quartz are expected to present extremely low dissolution rates on the order of $10^{-13}$ to $10^{-15}$ mol/cm$^2$/s. Hence, the solution contact times were extended to several days (~200 h) in order to minimize uncertainties in measurements of surface retreat.

3.2.1.1 Quartz (SiO$_2$)

Figure 17 shows the dissolution rates of quartz—before and following their irradiation. [17] It is noted that the dissolution rates of quartz increased significantly by ~3 orders of magnitudes after irradiation, indicating that the chemical stability of quartz is significantly affected following irradiation. The close equivalence in the dissolution rates of amorphous silica and irradiated quartz (Figure 17) suggests that the latter may be disordered to full amorphization under radiation exposure. It has been shown that dissolution typically originates from high structural defects and impurities sites; herein, for compounds such as amorphous silica, the lack of atomic periodicity/structural disorder implicates the alteration of the dissolution rates. [17] The extent of atomic structure alterations will be further discussed in Section 3.2.2.
3.2.1.2 Albite (NaAlSi₃O₈)

The dissolution rates of pristine and irradiated albite were acquired at far from equilibrium conditions. [46] This was ascertained by quantifying $\Delta G_d$ of the solution by using the measured concentrations of albite’s solubilized species to calculate its saturation level in solution (i.e., $\text{IAP}/K_{sp}$). It was thus determined that $\Delta G_d < -60 \text{ kJ/mol}$ across the majority of dissolution scenarios selected, with only one dissolution scenario featuring a slightly lower absolute value of $\Delta G_d (-52 \text{ kJ/mol at 25°C and pH 10})$; see Figure 18a. The dissolution of albite is characterized by three regimes based on the dependence of rates with $\Delta G_d$: [47-49] (i) far from equilibrium ($\Delta G_d < -60 \text{ kJ/mol}$), in which dissolution rates are independent of $\Delta G_d$, (ii) transition equilibrium ($-60 \leq \Delta G_d \leq -25 \text{ kJ/mol}$), in which the dissolution rate changes sharply with $\Delta G_d$, and (iii) near-equilibrium conditions ($-25 \leq \Delta G_d \leq 0 \text{ kJ/mol}$), in which the rate varies less severely with $\Delta G_d$ as solution saturation is approached toward the asymptotic limit. Simply, since $\Delta G_d$ is an indicator of the proximity (or lack thereof) to equilibrium, analysis of $\Delta G_d$ helps confirm that the dissolution of albite is indeed independent of the saturation state of the solution. As such, albite dissolves at a near-constant rate. It has been suggested that, at far from equilibrium conditions, albite achieves steady-state dissolution rates in a time interval of $\geq 1$ day. [50] Therefore, herein, albite dissolution was sampled at intervals of exactly 2 days to ensure that steady-state rates were obtained.
Figure 18: (a) Dissolution rates of pristine albite assessed using VSI as the function of the undersaturation level of the solution ($\Delta G_d$, kJ/mol). (b) The far-from-equilibrium dissolution rates of pristine albite assessed using VSI at different temperatures and solution pH levels. In both (a, b), the dissolution rates, and undersaturation levels were assessed following 12 days of solution contact ensuring that dissolution rates sampled at shorter contact times were at “far-from-equilibrium”. (c) A representative comparison of dissolution rates of pristine and irradiated albite assessed using VSI as a function of time at $T = 25 \pm 1^\circ C$ and pH $= 13$. The dissolution rate of irradiated albite is around a factor of 15 higher than that of pristine albite (shown by the bidirectional arrow).

The dissolution rate of albite increases with increasing pH and temperature (Figure 18b), as also noted elsewhere. [51] Importantly, the trends of ($\log_{10}$) dissolution rate as a function of pH can be fitted by an equation of the form $y = mx + c$, wherein $m \approx 0.3$. Blum and Lasaga [52] reported that albite’s dissolution rate is proportional to the surface concentration of OH⁻ sites—and that the surface density of OH⁻ sites depends on the pH of the solution. In turn, since the density of negative sites on albite’s surface is noted to correlate with the solution pH with a slope of 0.3 ($m \approx 0.3$), it is expected that albite’s dissolution rate should show a similar scaling with the solution pH as shown in Figure 18b. This trend can also be applied for anorthite (CaAl₂Si₂O₈), which, like albite, is an aluminosilicate mineral belonging to the plagioclase feldspar series, as shown in Figure 19.

Figure 18c shows the dissolution rates of pristine and irradiated albite as a function of time at $25 \pm 1^\circ C$ and pH $= 13$. The dissolution rate of irradiated albite is systematically higher than that of its pristine counterpart. Moreover, fitting of the dissolution trends by an equation of the form $D_r = A \exp(B \cdot t)$, where $D_r$ is the dissolution rate and $A$ and $B$ are fitting constants, shows that the dissolution rate of irradiated albite is around 15 times higher compared to its pristine variant. Thus, a constant $y$ offset would superimpose the two dissolution trend lines. Indeed, this result (i.e., that irradiation results in a 15× increase in the dissolution rate) is consistently observed across all solution pH’s and reaction temperatures considered. This observation is also consistent with the results of Hamilton et al., [32] who showed that the dissolution rate of a “glass” compositionally equivalent to crystalline albite is higher than that of crystalline albite in alkaline solutions. This conclusion is also proved using FTIR, and show in Section 3.2.2.

Our dissolution rate of pristine albite at pH 12 is quantified as $8.5 \times 10^{-13}$ mol/cm²/s. This value is slightly higher than the dissolution rate reported by Chou and Wollast et al., [53] which is on the order of $10^{-14}$ mol/cm²/s. This difference can be due to factors including: (i) the presence of inclusions; (ii) the difference in composition, e.g., of Ca present, and the presence of other impurities; (iii) the presence of twinning that are often present in the plagioclase family; or (iv) exsolution lamellae. All these factors may affect the dissolution rate, likely increasing it, because impurity and defects act as high-energy sites that favor dissolution. [54]

3.2.1.3 Anorthite (CaAl₂Si₂O₈)

The measured dissolution rates for pristine anorthite at pH 12 are consistent with previously published values of $10^{-12}$ to $10^{-13}$ mol/cm²/s. [55] We note that the anorthite sample contains impurities—as confirmed by polarized light microscopy—and has a composition most closely matching labradorite plagioclase, as evidenced by X-ray diffraction. Although slight, an enhancement in dissolution rates by a factor of 1.3-1.5 times upon irradiation was observed (Figure
19). This is consistent with the minor change in the number of constraints upon irradiation, i.e., by only 0.11, a value that is much lower compared to the other silicate minerals investigated in this study (see Table 9).

![Figure 19: Dissolution rate of anorthite as a function of the solution pH. The logarithm of the dissolution rate exhibits a linear dependence on pH—with a slope of 0.3.](image)

3.2.1.4 Almandine (Fe₃Al₂Si₃O₁₂)

Irradiation-induced changes in dissolution rates were also studied for almandine. [56] Almandine was dissolved using a flow-through cell (in-line diffusion cell, PermeGear) [57] at 25 ± 1°C over a range of solvent pH levels. In addition to the alkaline solutions used in the experiments above, acidic solutions prepared by adding HCl into DI water were also used as reaction solutions. The solutions were pumped into the flow-through cell using Biologic LP controller (Bio-Rad) [58] at a flow rate of 13.5 mL/min to prevent solution supersaturation and consequent precipitation as shown in Figure 20a, which may interfere with the measurement of dissolution rates. [59] A previous study on almandine dissolution showed that the duration of solution contact time needed to reach steady state dissolution rates is varying with the fluid flow rates. [60] For a solution flow rate of 13.5 mL/min and a fluid cell volume of 0.708 mL, the time needed for a near-complete solution exchange is estimated to be 3 s. The constant renewal of the reaction solution is expected to minimize changes in the solution composition over time. The influence of dissolution rates on flow rate is shown in Figure 20b. We observed that the rate initially increased with increasing flow rate up to a point and then stabilized. Hence, obtaining the steady state dissolution rate using flow rates > 10 mL/min is reasonable. Given enough time, the dissolution approaches a steady state in which dissolution is congruent and the rate of release of all components reaches a constant value. [51]
Figure 20: (a) VSI images of pristine almandine surface reacted at a flow rate of 0.55 mL/min (slow flow rate) in pH 2 HCl and pH 12 NaOH solutions. Results show the formation of precipitates in the latter condition. (b) Dissolution rate of almandine as a function of flow rate. Beyond a flow rate of 8 mL/min the dissolution rate plateaus demonstrating a rate independence of flow rate. Herein, dissolution was measured at a flow rate of 13.5 mL/min. (c) The dissolution rates of pristine (blue circles) and irradiated (red circles) almandine as a function of pH, the logarithm of which shows a linear relationship with pH. The rates increase with both increasing and decreasing pH with respect to a minimum value of 5. In both cases, this line has a slope of 0.3–0.4, suggesting that the dissolution mechanisms are comparable. (d) The zeta potential of pristine almandine measured as a function of solution pH. The minimum dissolution rate of pristine almandine (c) occurs at the pH where the sum of the absolute value of surface charge (Al and Si) is minimized, i.e., minimum zeta potential.

The steady-state dissolution rates for pristine and irradiated almandine as a function of pH are presented in Figure 20c. The rates increase with increasing (alkaline) and decreasing (acidic) pH about a minimum pH of ~5-6. Further, it was shown that the pH in which minimum dissolution rates of pristine almandine is observed coincides with its point of zero charge (PZC), highlighting that attack of terminal cationic sites by potential determining species (H⁺ or OH⁻) is influential in dissolution. This observation is consistent with almandine’s zeta potential as a function of pH, as shown in Figure 20d. It is noted that the absolute value of zeta potential increases systematically in both acidic and basic regimes – about the pH of the point of zero charge (PZC), where the total
surface charges from Al and Si surface sites are presumably minimized, based on studies on quartz and aluminum oxide from Walther et al. [61] Therein, the minimum in the dissolution rate occurs at the pH where the absolute surface charge from Si in quartz or Al in aluminum oxide is minimized—i.e., pH 8.4 and pH 2.5 for corundum and quartz, respectively. [61] Since alkalis and alkaline earth cations tend to leach rapidly from the aluminosilicate surface and be replaced by protons, it is the residual Al and Si left on the surface that determines the PZC. [61,62] For example, in almandine (Al/Si = 0.67), the surface charge and dissolution minimum are observed at a pH between 4 and 6, as noted in Figure 20c.

Irradiated almandine dissolved slightly faster than pristine almandine, by a constant y offset as observed for albite. This suggests that the dissolution mechanisms that are prevalent in both acidic and alkaline conditions are similar for both irradiated and pristine samples (Figure 20). The dissolution rates of quartz and albite increased by factors of 1000 and 15. [17,46] These silicates both have a highly polymerized framework silicate structure. Although the increase in $n_c$ after irradiation is substantial, i.e., by 0.65, and higher than both quartz and albite, reactivity increased only by a factor of 1.5-2. This can be partly explained by its dissimilar silicate structure composed of isolated silica tetrahedra.

### 3.2.2 Atomic structure alteration

To assess the nature and extent of the structural alterations induced by irradiation, cross-sectional TEM and SAED patterns were acquired for quartz and the results are shown in Figure 21. The sharp diffraction maxima noted in the SAED pattern past the end-of-range regions (of Ar$^+$ implantation) of quartz ((II) in Figure 21) are not observed in SAED patterns of the corresponding ion-irradiated regions (Figure 21, (I)). Rather, a diffuse band is noted, which is indicative of complete amorphization. Thus, whereas carbonate minerals remain resistant to radiation damage (Figure 13), quartz reaches a fully disordered (“glassy”) state following ion-implantation under the same implantation dose. These results are consistent with the MD simulations above [T2]. Irradiation induces significant changes in the inter-tetrahedral (Si–O–Si) bond angles (around 7% decrease in the average bond angle value) while having no noticeable effect on the bond lengths. In the case of quartz, the number of constraints per atom decreased from 3.67 (stressed-rigid) to 2.9 (flexible state), which increase the quartz dissolution rates in 3 orders of magnitude following irradiation.

![Figure 21: Cross-sectional TEM images and corresponding selected area electron diffraction (SAED) patterns from the ion implanted regions (I) and past ion end-of-range (II) for quartz single crystal shows the amorphization of quartz.](image)
FTIR spectra of silicate minerals usually show peaks in two regions: (1) > 2500 cm\(^{-1}\), which corresponds to the vibrations induced by hydroxyl groups, and (2) < 1300 cm\(^{-1}\), which features vibrations of the silicate network. [63-65] Our analysis focuses on this latter wavenumber region. To carefully analyze the data, the FTIR spectrum of albite was separated and magnified into two groups: a low (450-to-800 cm\(^{-1}\)) and a high (800-to-1200 cm\(^{-1}\)) wavenumber region, as shown in Figure 22. It has been previously noted that these two spectral ranges exhibit peaks that are closely correlated with the structural features of silicate’s network and its degree of disorder. [14] The vibrational modes corresponding to each peak are listed in Table 7. [66-69] The two most obvious peaks in silicates are those centered at 450 cm\(^{-1}\) and 780 cm\(^{-1}\), [66] which represent the rocking motion of the Si–O–Si bridging oxygen (BO) in siloxane bonds and the bending of Si–O–Si bonds, respectively. In aluminosilicates, the peak centered at 650 cm\(^{-1}\) represents tetrahedral ring vibrations. [63-65] The presence of Na atoms in the network enables charge-compensation of 4-fold coordinated [AlO\(_4\)]\(^{5-}\) units or the depolymerization of the network through the formation of non-bridging oxygen (NBO) atoms. In turn, these structural features affect the vibration modes of the rest of the aluminosilicate network. [63-65] In particular, the peak centered at 540 cm\(^{-1}\) represents the coupling of the bending of O–Si–O bonds within [SiO\(_4\)]\(^{4-}\) tetrahedra and Na–O bonds. [63-65]

![Figure 22: Representative FTIR spectra of the albite samples in the: (a) lower wavenumbers region, and, (b) higher wavenumbers region.](image)

Upon irradiation, the peaks that are found in the wavenumber range of 450–800 cm\(^{-1}\) are systematically shifted toward lower wavenumbers, indicating a decrease in the degree of atomic ordering. [14] The same trend is observed in the case of peaks in the higher wavenumber region that correspond to Si-BO and Si-NBO bond stretching modes. The extent of (incremental) peak shift can be calculated as: \[ \Delta \omega = \omega_{\text{irradiated}} - \omega_{\text{pristine}} \], where, \( \Delta \omega \) is the difference in the degree of Al/Si ordering between the irradiated and pristine (reference) samples, [64] and \( \omega_{\text{pristine}} \) and \( \omega_{\text{irradiated}} \) represent the wavenumbers of a given vibrational mode in pristine and irradiated albite, respectively (see Table 7). Since the peak shift is related to the degree of disordering within the aluminosilicate network, in general, the magnitude of the peak shift or reduction in peak intensity, correlated directly with the extent of disorder in the structure. Specifically, it is suggested that, within the irradiated region, the damage to the atomic structure of albite (e.g., since Al–O–Si and Si–O–Si bonds are destabilized) eases the detachment of Al and Si atoms from the solid, resulting in a higher dissolution rate for irradiated albite vis-à-vis pristine albite. This alteration in atomic structure is reflected in the number of constraints per atom (nc), which decreased by 0.3. When applied to
the topological kinetic model introduced in [T2], an increase of around 15 times in dissolution rates is predicted.

<table>
<thead>
<tr>
<th>Reference peaks (cm⁻¹)</th>
<th>Vibration mode</th>
<th>Pristine albite</th>
<th>Irradiated albite</th>
<th>δω</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>Si-O-Si rocking (vibration of the bridging oxygen in the direction normal to the initial Si-O-Si plane).</td>
<td>463</td>
<td>461</td>
<td>2</td>
</tr>
<tr>
<td>540</td>
<td>Coupling of the bending of O-Si-O bonds within silicate tetrahedra and Na-O stretching</td>
<td>531</td>
<td>523</td>
<td>8</td>
</tr>
<tr>
<td>650</td>
<td>Tetrahedral ring vibration</td>
<td>648</td>
<td>645</td>
<td>3</td>
</tr>
<tr>
<td>780</td>
<td>Si-O-Si bending (vibration of the bridging oxygen in the direction perpendicular to Si-Si axis within the initial Si-O-Si plane).</td>
<td>761</td>
<td>759</td>
<td>2</td>
</tr>
<tr>
<td>900-1200</td>
<td>Bridging-stretching modes of SiO₄ tetrahedra</td>
<td>1096</td>
<td>1044</td>
<td>52</td>
</tr>
</tbody>
</table>

As in albite, all peaks of almandine shifted systematically to the lower wavenumber region, indicating that the structure became more disordered after irradiation (see Figure 23). [14] In almandine, there are 16 peaks present in the wavenumber range 400-1500 cm⁻¹. [70] Generally, SiO₄ tetrahedral features are found in the 800-1170 cm⁻¹ and 500-700 cm⁻¹ regions, [71] whereas AlO₆ octahedral features are found in the 500-700 cm⁻¹ range, and at 464 cm⁻¹. [71] However, the peaks for cations in the dodecahedral structure composed mostly of Fe²⁺, with minor Mg²⁺ and Ca²⁺ are located in low wavenumber region (100-300 cm⁻¹), [71] and are beyond the range of the FTIR instrument used in these measurements.
Figure 23: FTIR patterns averaged from measurements on at least 5 locations on pristine (blue) and irradiated (red) almandine surfaces showing the (a) lower wavenumber region (400-800 cm\(^{-1}\)), and the (b) higher wavenumber region (800-1200 cm\(^{-1}\)). The characteristic peaks in pristine and irradiated almandine are marked by dashed blue and red lines, respectively. The peak positions and shifts (\(\delta \omega\)) are given in Table 8.

Table 8: The relevant FTIR peak positions and the assignment of their corresponding vibration modes for aluminosilicates, and specifically pristine and irradiated almandine.

<table>
<thead>
<tr>
<th>Reference peak (cm(^{-1}))</th>
<th>Vibration mode</th>
<th>Pristine almandine</th>
<th>Irradiated almandine</th>
<th>(\delta \omega)</th>
</tr>
</thead>
<tbody>
<tr>
<td>470</td>
<td>Al translation against O in octahedra</td>
<td>471</td>
<td>463</td>
<td>8</td>
</tr>
<tr>
<td>570</td>
<td>Asymmetric bending modes of SiO(_4) intra-tetrahedra</td>
<td>566</td>
<td>557</td>
<td>9</td>
</tr>
<tr>
<td>650</td>
<td>Tetrahedral ring vibration</td>
<td>637</td>
<td>635</td>
<td>2</td>
</tr>
<tr>
<td>880-900</td>
<td>Asymmetric stretching modes of SiO(_4) intra-tetrahedra</td>
<td>897</td>
<td>885</td>
<td>12</td>
</tr>
<tr>
<td>970-1050</td>
<td>Asymmetric stretching modes of SiO(_4) intra-tetrahedra</td>
<td>963</td>
<td>947</td>
<td>16</td>
</tr>
</tbody>
</table>
4. **Summary**

The primary objective of this task is to clarify the effect of irradiation (induced by Ar\(^+\) ion implantation) to chemical reactivity, i.e., dissolution rates measured by VSI. The alterations in structure and chemical reactivity are investigated for silicates and carbonates typically found in aggregates used in nuclear power plant concrete. In this work, we have shown that the radiation damage on the atomic structures of silicates such as quartz is more severe than in carbonates, i.e., calcite and dolomite. This distinction can be explained by the dominantly ionic nature of bonding in carbonates and covalent bonding in quartz; the latter of which is less stable when irradiated. Further, we have demonstrated that mineral dissolution rates are strongly correlated with the alteration in atomic structure and the rigidity of the structural network as defined by the change in the number of constraints per atom, \(\Delta n_c\) (Table 9).

Smaller enhancements in dissolution rates are observed for the other silicates: albite, anorthite, and almandine. This can be explained by the presence of cations including Na, Al, Ca, and Fe, which results in a decreased relative percentage of covalent bonds and increase in ionic bonding. The unique behavior of almandine can be explained by its crystallographic structure. Indeed, unlike albite, anorthite, and quartz wherein the silicate tetrahedral groups are arranged in a three-dimensional framework structure, almandine comprises silicate groups that are isolated from each other. Our data suggest that the degree of connectivity of the structure, i.e., degree of polymerization, affects the mineral’s susceptibility for structural alterations. Particularly, a higher extent of polymerization results in a higher degree of radiation damage because of the higher packing density, which favors radiation-induced structural changes.

The outcomes of the study reveal that silicate minerals are expected to dissolve incrementally faster after irradiation. This is problematic as the dissolution of silica, water, and alkali ions all contribute in the formation of expansive alkali-silica reaction (ASR) gels, which could expand and induce physical damages such as microcracking in concrete structural elements in nuclear power plants, ultimately reducing their durability. On the other hand, carbonate minerals are largely unaffected upon irradiation.

<table>
<thead>
<tr>
<th>Crystallographic structure</th>
<th>Chemical composition</th>
<th>(\Delta n_c) [T2]</th>
<th>Dr [T3]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbonate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>Trigonal (R3c)</td>
<td>CaCO(_3)</td>
<td>0</td>
</tr>
<tr>
<td>Dolomite</td>
<td>Trigonal (R3)</td>
<td>CaMg(CO(_3))(_2)</td>
<td>0</td>
</tr>
<tr>
<td><strong>Silicate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>Trigonal (P321)</td>
<td>SiO(_2)</td>
<td>-0.617</td>
</tr>
<tr>
<td>Albite</td>
<td>Triclinic (C1)</td>
<td>NaAlSi(_3)O(_8)</td>
<td>-0.307</td>
</tr>
<tr>
<td>Anorthite</td>
<td>Triclinic (P1)</td>
<td>CaAl(_2)Si(_2)O(_8)</td>
<td>0.113</td>
</tr>
<tr>
<td>Almandine</td>
<td>Cubic (Ia3d)</td>
<td>Fe(_3)Al(_2)Si(<em>3)O(</em>{12})</td>
<td>-0.650</td>
</tr>
</tbody>
</table>

**Table 9:** Summary of all the work done in [T3a] mineral aggregate dissolution
1. Objectives

This milestone report presents the first comprehensive study of the thermodynamic properties of synthetic alkali-silica reaction gels with respect to composition, i.e., Na/Si, K/Si, Ca/Si and Al/Si molar ratios, and temperatures of 5°C, 25°C, and 45°C. Data of this nature provide key input for reactive-transport simulations which model chemo-mechanical manifestations of aggregate dissolution, and expansive product formation in concretes used in NPP and in other relevant cementitious systems.

2. Materials and methods

2.1 Synthesis of alkali-silica reaction gels

The alkali-silica reaction gels were synthesized by a direct reaction of a mixture of reactive silica and calcium sources with an alkali hydroxide (NaOH/KOH) solution. This method enables a greater control of the gel composition and homogeneity than the sol-gel method. [72-74] Gel having various compositions representing the end-members of a range of ASR gels reported in literature [73,75] were prepared. Figure 24 shows ternary plots of the gel compositions synthesized, wherein the range of elemental molar ratios are: Na/Si = 0.25-to-1.20, K/Si = 0.125 – 0.50, Ca/Si = 0-to-0.22 and Al/Si = 0.05. In general, 4.8 g (0.08 mol) of hydrophilic amorphous SiO₂ (Cab-o-sil, HS-5) and the required amount of Ca (in the form of CaO freshly prepared by calcining CaCO₃ at 1000°C for 4 h), and/or Al (in the form of Al(NO₃)₃·9H₂O) were added in 18 MΩ·cm deionized water to produce a slurry with a solid-to-liquid mass ratio of 0.4. All chemicals were of analytical reagent grade. This step was followed by addition of the appropriate amount of 12.5 M NaOH solution, which was prepared by adding ACS reagent grade NaOH salt in 18 MΩ·cm deionized water. The mixture was then vigorously stirred with the aid of magnetic stirring bars in sealed high-density polyethylene (HDPE) vessels for 24 h, and then evacuated to dryness over calcium chloride desiccant at 25°C.

2.2 Solubility measurements

To quantify its solubility, the dried gel was dispersed in 18 MΩ·cm deionized water at a solid-to-liquid ratio of 1:30 (mass basis) and cured at 5°C, 25°C, and 45°C in sealed HDPE bottles, with periodic agitation (vigorous manual shaking, two to three times per week) for 90 days. After 90 days, the supernatant solution was extracted and filtered using a syringe through a 0.1 µm nylon filter and diluted with 5% nitric acid. The aqueous elemental composition of the diluted aliquot was then determined by inductively coupled plasma-optical emission spectrometry (ICP-OES).
2.3 Characterization of alkali-silica reaction gels

The thermogravimetric (TG) analyses of synthesized ASR gels were performed using a PerkinElmer (Waltham, MA, USA) STA 6000 simultaneous thermal analyzer (TGA/DTG/DTA) with a Pyris data acquisition interface. The powder samples were heated under ultrahigh purity N₂ purge at a heating rate of 10°C/min over a temperature range of 35-to-975°C. During the heating step, the samples were first thermally equilibrated at 40°C for 60 minutes to gently remove excess water before heating to 975°C. The mass loss (TGA) and differential weight loss (DTG) patterns acquired were used to identify thermal decomposition behavior and water content of the gel.

Qualitative x-ray diffraction (XRD) analyses were carried out on the synthesized ASR gels using a Panalytical X’Pert Pro X-ray Powder Diffractometer in a θ–θ configuration using Cu Kα (λ = 1.54 Å) radiation. The powder samples were scanned between 2° and 50° (2θ) in continuous mode with an integrated step scan of 0.017° (2θ), using an X’celerator RTMS Scanning Detector. The time required for acquisition of XRD patterns was around 5 min. A fixed divergence slit of 1° was used during data acquisition. The density of the solid ASR gels was analyzed using a Micromeritics (Micromeritics Corporation, Norcross, GA, USA) AccuPyc II Pycnometer. This technique employs a gas displacement method using helium gas to accurately measure the solid volume and density. The molar compositions were examined using a field emission-scanning electron microscope (FE-SEM: FEI Nova Nano SEM 230) provisioned with a Thermo Scientific NORAN System 7 energy-dispersive x-ray spectrometer (EDS). Particulates were dispersed onto double-sided adhesive carbon tape held on an aluminum stub, and the samples were sputter-coated with gold to prevent charge accumulation. A spot size (d₀) of 3.0-to-4.5, a working distance of 6 mm, an accelerating voltage of 7-to-15 kV, and a magnification of 5000x were used across all the imaging routines. The compositions of the gels were determined by x-ray microanalysis (EDS) using a fast EDS detector (i.e., to mitigate issues of mobility of light elements under electron beam irradiation) as averaged over 50 discrete points. Fourier transform infrared (FTIR) spectra of samples were collected using the attenuated total reflection (ATR) approach, using a PerkinElmer Spectrum Two spectrometer equipped with a diamond cell. Spectra were collected in the mid-infrared region from 400-to-4000 cm⁻¹ at a resolution of 4 cm⁻¹.

Furthermore, a PerkinElmer Avio 200 ICP-OES was used to measure the concentrations of Si, Na, K, Ca, and Al in the extracted supernatant solution for the solubility studies. Argon of ultrahigh purity (99.999%) was used to purge the optics and for plasma generation. The set-up

![Figure 24](image-url)
parameters used are as follows: 1500 W radio frequency power, 1.0 L min⁻¹ of sample flow rate, 8 L min⁻¹ of plasma flow rate, 0.2 L min⁻¹ of auxiliary gas flow rate, 0.7 L min⁻¹ of nebulization gas flow rate, and a viewing distance of 15 mm. The solutions were introduced into the plasma using a concentric glass nebulizer (Meinhard, Golden CO, USA) with the aid of a peristaltic pump and S10 Autosampler (PerkinElmer) at a sample flow rate of 1.0 L min⁻¹. The spectra lines (wavelengths) of the elemental Na 589.592 nm, K 766.490 nm, Ca 317.933 nm, Al 396.153 nm, and Si 251.611 nm were measured. The mean of triplicate measurements of the aqueous elemental speciation was used in the quantification of the solubility as presented below.

The elemental molar ratios obtained by SEM-EDS and the mass percent of water lost between 40 and 600°C obtained by TG analysis were used to calculate the water content of the gels, using Equation (5).

\[
H_2O = \frac{TW(Na_2O \cdot MW_{Na_2O} + K_2O \cdot MW_{K_2O} + CaO \cdot MW_{CaO} + \frac{Al_2O_3 \cdot MW_{Al_2O_3}}{2} + SiO_2 \cdot MW_{SiO_2})}{(100 - TW) \cdot MW_{H_2O}}
\]  

(5)

where H₂O is the amount of water contained a given gel (mol), TW is the total water content (sum of evaporable and non-evaporable water), i.e., the mass percent of water lost between 40°C-to-600°C [76] and Na₂O, K₂O, CaO, Al₂O₃, and SiO₂ are the average quantities of these oxides in the gels (moles) as determined via SEM-EDS analyses and MW is the molecular weight (molar mass) of each oxide (g/mol).

3. **Estimation of thermodynamic properties**

The standard absolute isobaric heat capacity (C_p°) of the synthesized ASR gel end-members was estimated using the additivity method [77-80] and Equation (6), defined in terms of structurally-relevant amorphous SiO₂(am) and incorporating the other constituents: NaOH(s), KOH(s), Ca(OH)₂(s), Al(OH)₃(am) and H₂O(l). The C_p° of the constituent phases used in the estimation of heat capacities of the gels are given in Table 10. The method has been successfully applied to estimate the heat capacity of silicate minerals, [81] cement phases [78, 79] including calcium-silicate-hydrate (C-S-H) gel, and calcium-(alkali)-aluminosilicate hydrate (C-(N,K)A-S-H) gel which are relevant to highly alkaline cementitious systems. [80,82] However, this method is expected to produce relatively small errors due to the varying strength of bonding of water, which may be bound on the structure through either of the following forms: as hydrate, structural water or occurring in a hydroxyl group. [78,81]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂, am</td>
<td>-848.9</td>
<td>-903</td>
<td>41</td>
<td>44.5</td>
<td>29</td>
<td>83,84</td>
</tr>
<tr>
<td>NaOH</td>
<td>-379.6</td>
<td>-425.8</td>
<td>64.4</td>
<td>59.5</td>
<td>18.8</td>
<td>84,85</td>
</tr>
<tr>
<td>KOH</td>
<td>-378.9</td>
<td>-424.7</td>
<td>78.9</td>
<td>64.9</td>
<td>27.5</td>
<td>84,85</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>-897.0</td>
<td>-985</td>
<td>83</td>
<td>87.5</td>
<td>33</td>
<td>84</td>
</tr>
<tr>
<td>Al(OH)₃, am</td>
<td>-1143.2</td>
<td>-1281</td>
<td>70</td>
<td>93.0758</td>
<td>32</td>
<td>86</td>
</tr>
<tr>
<td>H₂O</td>
<td>-237.2</td>
<td>-286</td>
<td>69.9</td>
<td>75.4</td>
<td>18</td>
<td>87,88</td>
</tr>
</tbody>
</table>
\[
\text{Cp}^n(SiO}_2\text{)(Na}_2\text{O}_{a\cdot}(K_2\text{O})_{b\cdot}(CaO)_{c\cdot}(Al_2O_3)_{d\cdot}(H_2O)_e = \text{Cp}^n\text{SiO}_2\text{am} + 2a*\text{Cp}^n\text{NaOH}_{(s)} + 2b*\text{Cp}^n\text{KOH}_{(s)} + c*\text{Cp}^n\text{Ca(OH)}_2_{(s)} + 2d*\text{Cp}^n\text{Al(OH)}_3_{(am)} + (e - a - b - c - 3d/2)*\text{Cp}^n\text{H}_2\text{O}_{(aq)} \quad (6)
\]
where, \(a, b, c, d, \) and \(e\) are the respective stoichiometric coefficients of \(\text{Na}_2\text{O}, \text{K}_2\text{O}, \text{CaO}, \text{Al}_2\text{O}_3\) and \(\text{H}_2\text{O}\) in the ASR gel end-members.

The solubility product, \(\log K_{sp}\), was calculated using the chemical activities (mol·L\(^{-1}\)) of the species from the dissociation reactions (Table 15), generated from the general reaction shown in Equation (7).

\[
\text{(SiO}_2\text{)(Na}_2\text{O}_{a\cdot}(K_2\text{O})_{b\cdot}(CaO)_{c\cdot}(Al_2O_3)_{d\cdot}(H_2O)_e(s) \Leftrightarrow \text{SiO}_2^0_{(aq)} + 2a\text{Na}^+_{(aq)} + 2b\text{K}^+_{(aq)} + b\text{Ca}^{2+}_{(aq)} + 2c\text{AlO}_2^-_{(aq)} + 2(a + b + c - d)\text{OH}^-_{(aq)} + (e - a - b - c - 3d/2)\text{H}_2\text{O}^0_{(aq)} \quad (7)
\]

This reaction yields the relationship shown in Equation (8) for the solubility product, \(K_{sp}\), as a function of the chemical activities of the relevant ionic species:

\[
K_{sp} = \left\{\text{SiO}_2^0_{(aq)}\right\}^{1} * \left\{\text{Na}^+_{(aq)}\right\}^{2a} * \left\{\text{K}^+_{(aq)}\right\}^{2b} * \left\{\text{Ca}^{2+}_{(aq)}\right\}^{c} * \left\{\text{AlO}_2^-_{(aq)}\right\}^{2d} * \left\{\text{OH}^-_{(aq)}\right\}^{2(a+b+c-d)} * \left\{\text{H}_2\text{O}^0_{(l)}\right\}^{(e-a-b-c+d)} \quad (8)
\]

The activities and aqueous speciation of the \(\text{SiO}_2^0_{(aq)}, \text{Na}^+_{(aq)}, \text{K}^+_{(aq)}, \text{Ca}^{2+}_{(aq)}, \text{AlO}_2^-_{(aq)}, \text{OH}^-_{(aq)}\) and \(\text{H}_2\text{O}^0_{(l)}\) were calculated from the measured concentrations of Si, Na, K, Ca and Al (Tables 11-13), charged balanced by \(\text{OH}^-\) with the aid of the geochemical speciation code, GEM-Selektor 3 (Gibbs Energy Minimization Software, GEMS version 3.3), [89] using the built-in PSI/Nagra 12/07 database [88] and other relevant GEMS databases. [78,80,86,90,91]
### Table 12: Solubility data of ASR gels at 25°C.

<table>
<thead>
<tr>
<th>Chemical formula of gel</th>
<th>( \log K_{sp} )</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Al</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SiO}<em>2 \cdot (\text{NaO})</em>{0.125} \cdot (\text{CaO})_{0.22} \cdot (\text{AlO}<em>2)</em>{0.025} \cdot (\text{H}<em>2\text{O})</em>{1.28} )</td>
<td>-9.353</td>
<td>6.07E-02</td>
<td>-</td>
<td>4.68E-04</td>
<td>5.32E-06</td>
<td>8.89E-03</td>
</tr>
<tr>
<td>( \text{SiO}<em>2 \cdot (\text{NaO})</em>{0.25} \cdot (\text{CaO})_{0.11} \cdot (\text{AlO}<em>2)</em>{0.025} \cdot (\text{H}<em>2\text{O})</em>{1.47} )</td>
<td>-8.026</td>
<td>1.14E-01</td>
<td>-</td>
<td>9.67E-05</td>
<td>3.15E-05</td>
<td>7.84E-02</td>
</tr>
<tr>
<td>( \text{SiO}<em>2 \cdot (\text{NaO})</em>{0.25} \cdot (\text{CaO})_{0.22} \cdot (\text{AlO}<em>2)</em>{0.025} \cdot (\text{H}<em>2\text{O})</em>{1.41} )</td>
<td>-9.14</td>
<td>9.77E-02</td>
<td>-</td>
<td>7.29E-05</td>
<td>1.43E-05</td>
<td>6.04E-02</td>
</tr>
</tbody>
</table>

*(a)*Calculated from the solubility in mol L⁻¹ of Na, K, Ca, Al and Si dissolved from the solid gel at stated temperature. The relative percent standard deviations are generally < 3 %.
## Table 13: Solubility data of ASR gels at 45°C.

<table>
<thead>
<tr>
<th>Chemical formula of gel</th>
<th>( \log K_{sp} ) (a)</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Al</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂·(Na₂O)₀.₁₂₅·(H₂O)₀.₄₉</td>
<td>-2.89</td>
<td>8.27E-02</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.07E-01</td>
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<tr>
<td>SiO₂·(Na₂O)₀.₁₂₅·(CaO)₀.₁₁·(H₂O)₀.₆₃</td>
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<td>1.20E-04</td>
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<td>5.97E-02</td>
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<td>-6.12</td>
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<td>-</td>
<td>1.44E-04</td>
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<tr>
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<td>-7.02</td>
<td>1.21E-01</td>
<td>-</td>
<td>1.47E-04</td>
<td>-</td>
<td>1.32E-01</td>
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<tr>
<td>SiO₂·(Na₂O)₀.₆₀·(H₂O)₀.₃₂</td>
<td>-6.58</td>
<td>1.26E+00</td>
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<td>-</td>
<td>-</td>
<td>1.55E+00</td>
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<tr>
<td>SiO₂·(Na₂O)₀.₆₀·(CaO)₀.₁₁·(H₂O)₀.₂₁</td>
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<td>7.83E-01</td>
<td>-</td>
<td>5.19E-03</td>
<td>-</td>
<td>9.12E-01</td>
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<tr>
<td>SiO₂·(Na₂O)₀.₆₀·(CaO)₀.₂₂·(H₂O)₀.₀₅</td>
<td>-7.52</td>
<td>9.55E-01</td>
<td>-</td>
<td>1.14E-03</td>
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<td>9.10E-01</td>
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<tr>
<td>SiO₂·(K₂O)₀.₀₆₃·(H₂O)₀.₅₇</td>
<td>-2.81</td>
<td>-</td>
<td>3.01E-02</td>
<td>-</td>
<td>-</td>
<td>3.55E-02</td>
</tr>
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<td>SiO₂·(K₂O)₀.₀₆₃·(CaO)₀.₁₁·(H₂O)₀.₀₂</td>
<td>-4.79</td>
<td>-</td>
<td>2.45E-02</td>
<td>1.35E-04</td>
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<td>SiO₂·(K₂O)₀.₀₆₃·(CaO)₀.₁₁·(H₂O)₀.₀₃</td>
<td>-5.84</td>
<td>-</td>
<td>1.96E-02</td>
<td>1.09E-04</td>
<td>-</td>
<td>1.68E-02</td>
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<tr>
<td>SiO₂·(K₂O)₀.₀₆₃·(CaO)₀.₁₁·(H₂O)₀.₆₇</td>
<td>-2.84</td>
<td>-</td>
<td>7.02E-02</td>
<td>-</td>
<td>-</td>
<td>9.09E-01</td>
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<td>SiO₂·(K₂O)₀.₁₂₅·(CaO)₀.₁₁·(H₂O)₀.₇₆</td>
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<td>-</td>
<td>5.06E-02</td>
<td>9.07E-05</td>
<td>-</td>
<td>5.42E-02</td>
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<tr>
<td>SiO₂·(K₂O)₀.₁₂₅·(CaO)₀.₁₁·(H₂O)₀.₈₁</td>
<td>-6.04</td>
<td>-</td>
<td>4.04E-02</td>
<td>3.66E-05</td>
<td>-</td>
<td>3.97E-02</td>
</tr>
<tr>
<td>SiO₂·(K₂O)₀.₁₂₅·(CaO)₀.₁₁·(H₂O)₀.₉₉</td>
<td>-3.36</td>
<td>-</td>
<td>1.56E-01</td>
<td>-</td>
<td>-</td>
<td>2.54E-01</td>
</tr>
<tr>
<td>SiO₂·(K₂O)₀.₁₂₅·(CaO)₀.₁₁·(H₂O)₀.₁₂</td>
<td>-5.06</td>
<td>-</td>
<td>9.80E-02</td>
<td>1.27E-04</td>
<td>-</td>
<td>1.31E-01</td>
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<td>SiO₂·(K₂O)₀.₁₂₅·(CaO)₀.₁₁·(H₂O)₀.₁₃</td>
<td>-6.46</td>
<td>-</td>
<td>1.02E-01</td>
<td>4.57E-05</td>
<td>-</td>
<td>1.19E-01</td>
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<tr>
<td>SiO₂·(Na₂O)₀.₁₂₅·(H₂O)₀.₁₉</td>
<td>-6.788</td>
<td>7.87E-02</td>
<td>-</td>
<td>3.62E-04</td>
<td>2.90E-06</td>
<td>1.40E-02</td>
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<tr>
<td>SiO₂·(Na₂O)₀.₁₂₅·(H₂O)₀.₁₈</td>
<td>-8.167</td>
<td>6.81E-02</td>
<td>-</td>
<td>5.20E-04</td>
<td>1.54E-06</td>
<td>1.09E-02</td>
</tr>
<tr>
<td>SiO₂·(Na₂O)₀.₁₂₅·(H₂O)₀.₁₇</td>
<td>-6.693</td>
<td>1.20E-01</td>
<td>-</td>
<td>7.59E-05</td>
<td>1.40E-05</td>
<td>8.04E-02</td>
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<tr>
<td>SiO₂·(Na₂O)₀.₁₂₅·(H₂O)₀.₁₆</td>
<td>-7.738</td>
<td>1.08E-01</td>
<td>-</td>
<td>7.58E-05</td>
<td>1.02E-05</td>
<td>6.74E-02</td>
</tr>
</tbody>
</table>

(a) Calculated from the solubility in mol·L⁻¹ of Na, K, Ca, Al and Si dissolved from the solid gel at stated temperature. The relative percent standard deviations are generally < 3 %.

The standard molar thermodynamic properties of relevant aqueous chemical species at \( T = 25°C \) and \( p = 1 \) bar as used in the thermodynamic calculations are presented in Table 14. The activity coefficient of the species was calculated using the Truesdell-Jones modification of the extended Debye-Hückel equation (Equation 9), [92] to account for the effects of solution non-ideality.

\[
\log \gamma_j = \frac{-A_j z_j^2 \sqrt{I}}{1 + b \alpha_j \sqrt{I}} + \log_{10} \frac{x_{jw}}{X_w}
\]  

(9)

where, \( \gamma_j \) is the activity coefficient of \( j^{th} \) ion (unitless); \( z_j \) is the charge of \( j^{th} \) ion; \( \alpha_j \) is the ion-size parameter (i.e., effective hydrated diameter of \( j^{th} \) ion; \( \alpha_j = 3.31 \) Å for NaOH-dominated solution, and 3.67 Å for KOH-dominated solution); \( I \) (kg \( 1/2 \)·mol\( -1/2 \)) and \( B \) (kg \( 1/2 \)·mol\( -1/2 \)·m\( -1 \)) are \( T,P \)-dependent Debye-Hückel electrostatic parameters; \( b \) is a semi-empirical parameter that describes short-range interactions between charged aqueous species in an electrolyte solution (representing the predominant electrolyte in the system; \( b = 0.098 \) kg·mol\( -1 \) for NaOH-dominated solution, and 0.123 kg·mol\( -1 \) for KOH-dominated solution); \( I \) is the molal ionic strength of the solution (mol·kg\( -1 \)); \( x_{jw} \) is the molar quantity of water, and \( X_w \) is the total molar amount of the aqueous phase. The model also accounted for changes in the activity of water based on the osmotic coefficient; although consideration of the osmotic coefficient, very slightly, if at all altered the ion activities. It should be noted that the applied solution phase model is accurate only for \( I \leq 2.0 \) mol/kg beyond which its accuracy is reduced. [94,95] Also, the description of aqueous silicate
speciation in the GEMS databases does not currently extend beyond dimeric silicate and aluminosilicate units, and adsorption of aqueous species onto solid phases is also not fully considered. Therefore, while the Truesdell-Jones form of the extended Debye–Hückel equation (which is directly encoded in GEM-Selektor) was chosen here as a first step in the development of the thermodynamic model for ASR gel, future efforts will be directed towards the incorporation of a complete description for effect of sorption and silica oligomerization, and the use of improved models applicable at higher ionic strengths such as the Pitzer model.

Table 14: Standard partial molar thermodynamic properties of the aqueous species used in the calculations of solubility constants.

<table>
<thead>
<tr>
<th>Species</th>
<th>(\Delta G^\circ) [kJ mol(^{-1})]</th>
<th>(\Delta H^\circ) [kJ mol(^{-1})]</th>
<th>(S^\circ) [J mol(^{-1}) K(^{-1})]</th>
<th>(C_p^\circ) [J mol(^{-1}) K(^{-1})]</th>
<th>(V^\circ) [cm(^3) mol(^{-1})]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(^3+)</td>
<td>-483.7</td>
<td>-530.6</td>
<td>-325.1</td>
<td>-128.7</td>
<td>-45.2</td>
<td>90</td>
</tr>
<tr>
<td>AlO(^-) (+ H(_2)O = Al(OH)(_2)(^+))</td>
<td>-690.6</td>
<td>-713.6</td>
<td>-113.0</td>
<td>-126.1</td>
<td>-0.3</td>
<td>90</td>
</tr>
<tr>
<td>AlO(^2-) (+ 2H(_2)O = Al(OH)(_3)(^+))</td>
<td>-827.5</td>
<td>-925.6</td>
<td>-30.2</td>
<td>-48.9</td>
<td>9.5</td>
<td>90</td>
</tr>
<tr>
<td>AlOOH(^+) (+ 2 H(_2)O = Al(OH)(_3)(^+))</td>
<td>-864.3</td>
<td>-947.1</td>
<td>-40.3</td>
<td>-209.2</td>
<td>-13.0</td>
<td>90</td>
</tr>
<tr>
<td>AIOH(^2+)</td>
<td>-692.6</td>
<td>-767.3</td>
<td>-184.9</td>
<td>56.0</td>
<td>-2.7</td>
<td>90</td>
</tr>
<tr>
<td>AIHSiO(_3)(^2+) (+ H(_2)O = AlSiO(OH)(_3)(^+))</td>
<td>-1540.5</td>
<td>-1634.3</td>
<td>-25.0</td>
<td>-215.9</td>
<td>0</td>
<td>87,88</td>
</tr>
<tr>
<td>AlSiO(_3)(^2+) (+ 3H(_2)O = AlSiO(OH)(_6)(^-))</td>
<td>-1681.4</td>
<td>-1833.9</td>
<td>11.1</td>
<td>-4.5</td>
<td>87,88</td>
<td></td>
</tr>
<tr>
<td>Ca(^2+)</td>
<td>-552.8</td>
<td>-543.1</td>
<td>-56.5</td>
<td>-30.9</td>
<td>-18.4</td>
<td>90</td>
</tr>
<tr>
<td>CaOH(^+)</td>
<td>-717.0</td>
<td>-751.6</td>
<td>28.0</td>
<td>6.0</td>
<td>5.8</td>
<td>90</td>
</tr>
<tr>
<td>Ca(HSiO(_3))(^+) (+ H(_2)O = CaSiO(OH)(_3)(^+))</td>
<td>-1574.2</td>
<td>-1686.5</td>
<td>-8.3</td>
<td>137.8</td>
<td>-6.7</td>
<td>99</td>
</tr>
<tr>
<td>CaSiO(_3)(^2+) (+ H(_2)O = CaSiO(OH)(_6)(^-))</td>
<td>-1517.6</td>
<td>-1686.8</td>
<td>-136.7</td>
<td>88.9</td>
<td>15.7</td>
<td>78</td>
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<tr>
<td>K(^+)</td>
<td>-282.5</td>
<td>-252.1</td>
<td>101</td>
<td>8.4</td>
<td>9.0</td>
<td>90</td>
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<tr>
<td>KOH(^-)</td>
<td>-437.1</td>
<td>-474.1</td>
<td>108.4</td>
<td>-85</td>
<td>15.0</td>
<td>90</td>
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<tr>
<td>Na(^+)</td>
<td>-261.9</td>
<td>-240.3</td>
<td>58.4</td>
<td>38.1</td>
<td>-1.2</td>
<td>90</td>
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<tr>
<td>NaOH(^0)</td>
<td>-418.1</td>
<td>-470.1</td>
<td>44.8</td>
<td>-13.4</td>
<td>3.5</td>
<td>90</td>
</tr>
<tr>
<td>NaHSiO(_3)(^0)</td>
<td>-1288.2</td>
<td>-1407.9</td>
<td>41.8</td>
<td>102.9</td>
<td>-127.9</td>
<td>90</td>
</tr>
<tr>
<td>HSiO(_3)(^-) (+ H(_2)O = SiO(OH)(_3)(^-))</td>
<td>-1014.6</td>
<td>-1144.7</td>
<td>20.9</td>
<td>8.7</td>
<td>4.5</td>
<td>99</td>
</tr>
<tr>
<td>SiO(_2)(^0) (+ 2H(_2)O = Si(OH)(_4)(^0))</td>
<td>-833.4</td>
<td>-887.9</td>
<td>41.3</td>
<td>44.5</td>
<td>16.1</td>
<td>-83,100</td>
</tr>
<tr>
<td>SiO(_2)(^0) (+ 2H(_2)O = Si(OH)(_4)(^0))</td>
<td>-3600.8</td>
<td>-4082.7</td>
<td>-253.9</td>
<td>-1123.2</td>
<td>0</td>
<td>87,88</td>
</tr>
<tr>
<td>SiO(_2)(^0) (+ H(_2)O = SiO(OH)(_2)(^0))</td>
<td>-938.5</td>
<td>-1098.7</td>
<td>-80.2</td>
<td>119.8</td>
<td>34.1</td>
<td>78</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>-157.3</td>
<td>-230.0</td>
<td>10.7</td>
<td>-136.3</td>
<td>-4.7</td>
<td>90</td>
</tr>
<tr>
<td>H(^+)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>90</td>
</tr>
<tr>
<td>H(_2)O(^0)</td>
<td>-237.2</td>
<td>-285.9</td>
<td>69.9</td>
<td>75.4</td>
<td>18.1</td>
<td>91</td>
</tr>
<tr>
<td>N(_2)(^0)</td>
<td>18.2</td>
<td>-10.4</td>
<td>95.8</td>
<td>234.2</td>
<td>33.4</td>
<td>100</td>
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<tr>
<td>O(_2)(^0)</td>
<td>16.4</td>
<td>-12.2</td>
<td>109.0</td>
<td>234.1</td>
<td>30.5</td>
<td>100</td>
</tr>
</tbody>
</table>

The Gibbs energy effect of reaction, \(\Delta_r G_t^\circ\), at temperature T was computed using Equation (10), given by:

\[
\Delta_r G_t^\circ = -RT \ln K_{sp(T)}
\]

where \(R = 8.31451 \text{ J mol}^{-1} \text{K}^{-1}\) is the universal gas constant and \(K_T\) is the equilibrium solubility product at a given temperature.

The temperature dependence of the logarithm of the solubility product, \(\log K_{sp(T)}\), was calculated from the activities obtained at 5°C, 25°C, and 45°C, using the dissociation reaction shown in Table 15, with the aid of the built-in three-term temperature extrapolation in GEM-Selektor (Equation 11).

\[
\log K_{sp(T)} = A_0 + A_2 T^{-1} + A_3 \ln T
\]

where

\[
A_0 = \frac{0.4343}{R} \cdot [\Delta_r S_{T_0}^0 - \Delta_r C_{pT_0}^0 (1 + \ln T_0)]
\]
\[ A_2 = -0.4343 \cdot \left( \Delta_r H^0 - \Delta_r C p^0 T_0 \right) \]  
\[ A_3 = \frac{0.4343 R}{T_0} \cdot \Delta_r C p^0 \]  
\[ \Delta_r S^0_T = \Delta_r S^0_{T_0} + \Delta_r C p^0_{T_0} \ln \frac{T}{T_0} \]  
\[ \Delta_r H^0_T = \Delta_r H^0_{T_0} + \Delta_r C p^0_{T_0} (T - T_0) \]  
\[ \Delta_r G^0_T = \Delta_r H^0_{T_0} - T \Delta_r S^0_T \]  

where, \( A_0, A_2 \) and \( A_3 \) are empirical constants, \( T_0 \) is the reference temperature (25°C), \( \Delta_r C p^0 \) is the heat capacity effect of reaction at temperature \( T \), \( \Delta_r H^0 \) is the enthalpy effect of reaction at temperature \( T \), \( \Delta_r S^0 \) is the entropy effect of reaction at temperature \( T \), \( \Delta_r G^0 \) is the Gibbs free energy effect of reaction at temperature \( T \).

The Gibbs free energy effect of reaction at standard state (25°C and 1 bar pressure), \( \Delta_r G^0_{T_0} \), was calculated using Equation (10), and the enthalpy effect of reaction at standard state, \( \Delta_r H^0_{T_0} \), was estimated to obtain the best-fit extrapolated solubility products according to Equations (11-16), while assuming that the heat capacity effect of reaction, \( \Delta_r C p^0_T = \Delta_r C p^0_{T_0} = \Delta a_0 \), is constant over the temperature range of 0–100°C. The entropy effect of reaction at standard state, \( \Delta_r S^0_{T_0} \), was calculated using Equation (17). With the aid of the software GEMS, the standard molar thermodynamic properties: Gibbs free energy of formation (\( \Delta f G^0 \)), enthalpy of formation (\( \Delta f H^0 \)) and entropy of formation (\( S^0 \)) at 25 and 1 bar, were calculated following the dissolution reactions shown in Table 15 and the estimated \( \Delta_r G^0_{T_0}, \Delta_r H^0_{T_0} \) and \( \Delta_r S^0_{T_0} \). Lastly, the molar volume, \( V^0 \), was estimated from the measured density and molar mass (calculated from its theoretical composition) of the ASR gels.
Table 15: The dissolution reactions and calculated solubility products at 5°C, 25°C, and 45°C of alkali-silica reaction gels having various compositions.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Gel composition (molar ratio)</th>
<th>Measured Chemical formula of gel</th>
<th>Dissociation products used to calculate solubility products</th>
<th>Reaction products used to estimate heat capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>N125</td>
<td>0.25 0 N/A</td>
<td>SiO₂⁻·(Na₂O)₀.₁₂₅⁻·(H₂O)₀.₄₉</td>
<td>SiO₂⁻⁻(aq) + 0.25 Na⁺⁻(aq) + 0.25 OH⁻⁻(aq) + 0.365 H₂O(l)</td>
<td>SiO₂(αs) + 0.25 NaOH + 0.365 H₂O</td>
</tr>
<tr>
<td>N125C1</td>
<td>0.25 0.11 N/A</td>
<td>SiO₂⁻·(Na₂O)₀.₁₂₅⁻·(CaO)₀.₁₁⁻·(H₂O)₀.₆₃</td>
<td>SiO₂⁻⁻(aq) + 0.25 Na⁺⁻(aq) + 0.11 Ca²⁺⁻(aq) + 0.47 OH⁻⁻(aq) + 0.395 H₂O(l)</td>
<td>SiO₂(αs) + 0.25 NaOH + 0.11 Ca(OH)₂ + 0.395 H₂O</td>
</tr>
<tr>
<td>N125C2</td>
<td>0.25 0.22 N/A</td>
<td>SiO₂⁻·(Na₂O)₀.₁₂₅⁻·(CaO)₀.₂₂⁻·(H₂O)₀.₇₂</td>
<td>SiO₂⁻⁻(aq) + 0.25 Na⁺⁻(aq) + 0.22 Ca²⁺⁻(aq) + 0.69 OH⁻⁻(aq) + 0.375 H₂O(l)</td>
<td>SiO₂(αs) + 0.25 NaOH + 0.22 Ca(OH)₂ + 0.375 H₂O</td>
</tr>
<tr>
<td>N25</td>
<td>0.5 0 N/A</td>
<td>SiO₂⁻·(Na₂O)₀.₂₅⁻·(H₂O)₀.₂₂</td>
<td>SiO₂⁻⁻(aq) + 0.5 Na⁺⁻(aq) + 0.5 OH⁻⁻(aq) + 0.97 H₂O(l)</td>
<td>SiO₂(αs) + 0.5 NaOH + 0.97 H₂O</td>
</tr>
<tr>
<td>N25C1</td>
<td>0.5 0.11 N/A</td>
<td>SiO₂⁻·(Na₂O)₀.₂₅⁻·(CaO)₀.₁₁⁻·(H₂O)₀.₄₁</td>
<td>SiO₂⁻⁻(aq) + 0.5 Na⁺⁻(aq) + 0.11 Ca²⁺⁻(aq) + 0.72 OH⁻⁻(aq) + 0.78 H₂O(l)</td>
<td>SiO₂(αs) + 0.5 NaOH + 0.11 Ca(OH)₂ + 0.78 H₂O</td>
</tr>
<tr>
<td>N25C2</td>
<td>0.5 0.22 N/A</td>
<td>SiO₂⁻·(Na₂O)₀.₂₅⁻·(CaO)₀.₂₂⁻·(H₂O)₀.₀₈</td>
<td>SiO₂⁻⁻(aq) + 0.5 Na⁺⁻(aq) + 0.22 Ca²⁺⁻(aq) + 0.94 OH⁻⁻(aq) + 0.61 H₂O(l)</td>
<td>SiO₂(αs) + 0.5 NaOH + 0.22 Ca(OH)₂ + 0.61 H₂O</td>
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<td>SiO₂⁻·(Na₂O)₀.₆₀⁻·(H₂O)₀.₃₂</td>
<td>SiO₂⁻⁻(aq) + 1.2 Na⁺⁻(aq) + 1.2 OH⁻⁻(aq) + 2.72 H₂O(l)</td>
<td>SiO₂(αs) + 1.2 NaOH + 2.72 H₂O</td>
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<td>SiO₂⁻·(Na₂O)₀.₆₀⁻·(CaO)₀.₁₁⁻·(H₂O)₀.₂₁</td>
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<tr>
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<td>1.2 0.22 N/A</td>
<td>SiO₂⁻·(Na₂O)₀.₆₀⁻·(CaO)₀.₂₂⁻·(H₂O)₀.₀₅</td>
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<td>SiO₂⁻·(K₂O)₀.₁₂₅⁻·(CaO)₀.₁₁⁻·(H₂O)₀.₁₂</td>
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<td>SiO₂⁻⁻(aq) + 0.25 Na⁺⁻(aq) + 0.11 Ca²⁺⁻(aq) + 0.05 AlO₂⁻⁻(aq) + 0.42 OH⁻⁻(aq) + 0.98 H₂O(l)</td>
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SiO2(Na2O)0.125(CaO)0.22(Al2O3)0.025(H2O)0.49
SiO2°(aq) + 0.25 Na+(aq) + 0.22 Ca2+(aq) + 0.05 AlO2-(aq) + 0.64 OH-(aq) + 0.96 H2O(l)
SiO2(aq) + 0.25 NaOH + 0.22 Ca(OH)2 + 0.05 Al(OH)3 + 0.86 H2O

N25C1A025 0.5 0.11 0.05
SiO2(Na2O)0.25(CaO)0.11(Al2O3)0.025(H2O)0.6
SiO2°(aq) + 0.5 Na+(aq) + 0.11 Ca2+(aq) + 0.05 AlO2-(aq) + 0.67 OH-(aq) + 1.13 H2O(l)
SiO2(aq) + 0.5 NaOH + 0.11 Ca(OH)2 + 0.05 Al(OH)3 + 1.03 H2O

N25C2A025 0.5 0.22 0.05
SiO2(Na2O)0.25(CaO)0.22(Al2O3)0.025(H2O)1.19
SiO2°(aq) + 0.5 Na+(aq) + 0.22 Ca2+(aq) + 0.05 AlO2-(aq) + 0.89 OH-(aq) + 1.96 H2O(l)
SiO2(aq) + 0.5 NaOH + 0.22 Ca(OH)2 + 0.05 Al(OH)3 + 0.86 H2O

(a) The standard deviations in measured Na/Si, K/Si, Ca/Si and Al/Si molar ratios are ± 0.05, ± 0.04, ± 0.02, and ± 0.01, respectively; (b) M represents either Na or K.

<table>
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<th>Chemical formula of gel</th>
<th>log 𝐾 oe</th>
<th>ΔG°</th>
<th>ΔH°</th>
<th>S°</th>
<th>Cp°</th>
<th>Fitting parameters for log 𝐾 oe (unitless)(b)</th>
<th>V°(c)</th>
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<td>SiO2(Na2O)0.125(H2O)0.49</td>
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<td>145.71</td>
<td>86.85</td>
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<td>-1155.6</td>
<td>-1240.1</td>
<td>129.0</td>
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<td>112.9</td>
<td>163.31</td>
<td>718.88</td>
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</table>

(a) Calculated from the solubility in mol·l⁻¹ units, (b) coefficients of the 'three-term temperature extrapolation of logarithm of solubility product: \(\log K_{sp(T)} = A_0 + A_2 T^{-1} + A_3 \ln T\) (Equation 11), [77,101,102] (c) Calculated from measured density (g·cm⁻³) and calculated molar mass (g·mol⁻¹) of ASR gel.
4. Results and Discussion

4.1 Characterization of synthesized alkali-silicate reaction gels

Figure 25a shows representative XRD patterns of synthesized ASR gels with compositions belonging to the sodium-silicate-hydrate (N-S-H) system (the complete set of XRD data is presented in Figures 26-28), showing the typical broad Bragg-scattering centered at $2\theta \approx 22.5^\circ$ corresponding to SiO$_2$, which generally shifts to higher angles with the introduction and exchange of cations such as Na, Ca, or Al. This indicates a decrease in the degree of silica polymerization [73] resulting from the hydrolysis of siloxane (Si–O) bonds connecting adjacent silica-tetrahedra and the subsequent bonding of the cation with the non-bridging oxygens (e.g., $\equiv$Si–O–Si$\equiv + 2$(Na$^+$, OH$^-$) $\rightarrow$ 2(Na–O–Si≡) + H$_2$O). [103,104] Hence, the degree of silica polymerization decreases with increasing alkali content of the gel. [73]

Figure 25b shows representative FTIR spectra of the synthesized ASR gels, showing the characteristic bands commonly reported for field ASR gel samples. [105] Particularly, the band centered around 512 cm$^{-1}$ and 780 cm$^{-1}$ corresponds to the bending and symmetric stretching of O–Si–O, respectively; the band centered around 940 cm$^{-1}$ is due to the stretching of X–O–Si (where X = Na, K or Ca), [105,106] and the major band centered at 1010 cm$^{-1}$ is due to the asymmetric and symmetric stretching of Si–O. [107-111] The band centered around 1640 cm$^{-1}$ is assigned to the bending of molecular H$_2$O in the gel, while the broad band extending from 2200 to 3700 cm$^{-1}$ arises from the stretching of X–OH, where X = H, Na, K or Si is bonded to the OH groups in the amorphous silica matrix. [112,113]

Moreover, Figure 25c displays a representative thermal decomposition profile of the synthesized gels, showing significant mass loss below 200°C which is typical of cementitious gel phases containing evaporable water, e.g., calcium silicate hydrate, C-S-H, [114] and sodium aluminum silicate hydrate N-A-S-H gels. [76]
Figure 26: XRD patterns of synthesized ASR gels with compositions in the sodium-calcium-silicate-hydrate system: (a) Ca/Si = 0, (b) Ca/Si = 0.11, and (c) Ca/Si = 0.22.

Figure 27: XRD patterns of synthesized ASR gels with compositions in the potassium-calcium-silicate-hydrate system, showing minor phase separated potassium-silicate hydrate which increases with increasing potassium and calcium content of gel.

Figure 28: XRD patterns synthesized ASR gels with compositions in the calcium-aluminum-silicate-hydrate system. Minor NaNO₃ crystals originate from the Al(NO₃)₃ precursor.

4.2 Effect of alkali and calcium-silicon contents on the thermodynamic property of ASR gel

The standard molar thermodynamic properties (i.e., log $K_p^o$, $\Delta G^o$, $\Delta H^o$, $S^o$, $Cp^o$ and $V^o$) of the synthesized ASR gels at 25°C and 1 bar are shown in Table 16 (the complete solubility data...
set for all temperatures investigated are presented in Tables 11-13. The solubility product indicates the dissolution-precipitation tendencies of a phase in water: lower $\log K_{\text{sp}}$ indicates that the gel is less soluble, i.e., more likely to precipitate under appropriate conditions, whereas higher $\log K_{\text{sp}}$ indicates that a gel is more soluble and that its precipitation is relatively less favored. [79,95] The values of $\log K_{\text{sp}}$ of ASR gels as a function of Ca/Si and Na/Si molar ratios are displayed in Figure 29, showing that solubility decreases with increasing Ca/Si and Na/Si up to about Na/Si = 1.2 and Ca/Si = 0.11. At higher Na and Ca contents, (e.g., Na/Si = 1.20 and Ca/Si = 0.22), a different trend was observed; the solubility either remained near constant, or increased slightly (Figures 29a and 29b). High Na composition of this nature (Na/Si = 1.2) is not typical of field ASR gel samples, [73,75] and is generally only relevant at early ages. Nonetheless, as seen in Figure 30c the solubility of Na-based gels decreases with increasing (Na+Ca)/Si, overall.

Conversely, $\log K_{\text{sp}}$ do not vary significantly with respect to K/Si (Figures 29d and 29e). Figures 29c and 29f show the combined effect of Na and Ca content on the solubility product constants of ASR gels, wherein it is clearly seen that the dependence of $\log K_{\text{sp}}$ on (Na+Ca)/Si is more significant than on (K+Ca)/Si.

Interestingly, the observed difference in the effect of Na and K contents on the solubility properties of ASR gel contradicts suggestions in the published literature wherein both alkali metals...
(Na and K) are often thought as having similar effects on the chemo-mechanical properties of ASR gel. [114] Nonetheless, some authors have reported differences in the ASR manifestations for concrete mixture systems having similar Na$_2$O$_{eq}$ but different K/Na ratios. [115] It is often observed that different concentrations of Na and K are required for ASR gel formation [117] but previous theory on the mechanism of ASR gel formation [102,103] has explained neither this observation nor the reason for the higher sodium than potassium contents in reported ASR gel. [75] Not until recently that Visser explained that this property arises from differences in the screening effect of the two cations, in which the “cation gelling strength” (described as related to the ability of the cation to screen the silicic acid anion) of K is higher than that of Na, such that a smaller amount of K is required for gelation compared to Na. [116] Visser explained that K shields the silicic acid more effectively than Na, owing to the higher effective charge of a hydrated K$^+$ ion than a hydrated Na$^+$ ion. On the basis of hydration, for cations of a similar valence, those having a larger ion radius (and more protons) bind molecular water more loosely and across a larger area resulting in a less shielded positive charge and higher effective charge of hydrated ion. [116] Thus, it is found that the concentration to bring about gelation follows the order of the effective charge of hydrated ions (similar to the so-called Hofmeister series [117,118]), e.g., for group 1 elements, gelation strength varies as follows: Li$<$Na$<$K$<$Cs$<$Rb. [116]

Therefore, cations will contribute to the cohesiveness and strength of the formed sol (gel) as observed by Iller, [119] and such contribution is reported to be weak for hydrated cations with a very weak effective charge such as Li$^+$ and Na$^+$. Hence it is appropriate to deduce that K$^+$ on account of its higher effective charge will be bound more strongly to the non-bridging oxygens of the silicate network, resulting in greater resistance to exchange by cations such as Ca$^{2+}$. This is in contrast with Na$^+$, which can be more readily exchanged by other cations. Since calcium has a higher effective charge and higher cation gelation strength, it produces gels which have a stronger screening effect on the silicic acid anion (i.e., stronger net electrostatic attractive force), and greater cohesion, leading to an overall lower solubility product as observed in Figure 30. This phenomenon may help explain why the solubility of K-based ASR gels does not vary significantly with gel composition, as opposed to Na-based gels.

![Figure 30: The solubility product of gels of composition, Na/Si = K/Si = 0.5 and Ca/Si = (a) 0, (b) 0.11, and (c) 0.22, showing a greater decrease in the solubility of the Na-based gels compared to those of the K-based gels, with respect to increasing Ca content.](image)

4.3 Temperature dependence of the solubility product of ASR gels
The evolution of $\log K_{sp}$ of the ASR gels as a function of the temperature of the aqueous solution is presented in Figure 31 for Ca/Si ratios ranging from 0-to-0.22, showing that as is typical of silicates, $\log K_{sp}$ increases with increasing temperature, albeit only slightly by a factor of up to 1.25 between 5°C and 45°C. As seen in Figure 31, the extent to which temperature affects solubility depends on the gel composition. Particularly, the influence of temperature on solubility increases with increasing Na/Si and Ca/Si as seen in Figure 31d. In other words, the temperature-dependence of the $\log K_{sp}$ is more pronounced at higher alkali and Ca contents.

The balance in kinetics and thermodynamics effects controls the dissolution-precipitation reactions during the thermochemical manifestation of ASR gel. [121,122] Previous studies have shown that both solubility and rate of silicate mineral dissolution in alkaline solutions increase with increasing temperature. [123-126] This observation on solubility dependence on temperature is consistent with the established $\log K_{sp}$ in this study. Given the relatively small effect of temperature on $\log K_{sp}$, it can be suggested that the effect of temperature on the kinetics of silica dissolution would dominantly control the approach to dissolution-precipitation equilibrium under appropriate conditions. [127]

![Figure 31: The solubility product, $\log K_{sp}$, as a function of temperature (5°C to 45°C), and composition for (a-c) Na-based gels and (d-f) K-based gels showing slight increases in $\log K_{sp}$ with increasing temperature. The temperature-dependence of $\log K_{sp}$ are fitted with the equation $\log K_{sp}(T) = A_0 + A_2 T^{-1} + A_3 \ln T$ (Equation 11). The error bars are estimated from the standard deviation of triplicate measurements of elemental concentrations.](image-url)
4.4 Examining the effect of aluminum on the solubility of ASR gel

Aluminum is seldom reported to be present in actual ASR gel samples from the field, in which Al content (relative to Si) is on the order of Al/Si (molar basis) \( \leq 0.05 \). [73] However, most cementitious systems are rich in alumina, and Al-rich supplementary cementitious materials (SCMs) are widely used to mitigate ASR. [127-129] Previous studies on the role of alumina in similar systems have mainly focused on the effect of Al-containing compounds (e.g., SCMs) on the dissolution kinetics of siliceous aggregates. In one study, Al contained in SCM was reported to reduce SiO\(_2\) dissolution rate, while not inducing alterations in the morphology, structure, and composition of reaction products. [130] Nonetheless, the role of Al in the precipitation and thermodynamics of ASR gels has remained unclear. [131] Here, synthetic Al-containing ASR gels with compositions in the SiO\(_2\)-Na\(_2\)O-CaO-Al\(_2\)O\(_3\)-H\(_2\)O (S-N-C-A-H) system, were also studied. Figure 32 displays the \( \log K_{sp} \) as a function of temperature for Al-free and corresponding Al-containing gel phases. Notably, the incorporation of Al in the gel leads to significantly reduced solubilities, by up to a factor of 1.7 (Figure 32a). In addition, the magnitude of such reduction evidently becomes greater at lower temperatures. Further, the influence of Al content on solubility is also affected by other compositional factors such as the Na and Ca content of the gel. In particular, as both Na and Ca contents of the gel increase, the influence of Al content on solubility diminishes.

![Figure 32](image_url)

**Figure 32:** Solubility products of Al-free and Al-containing ASR gels as a function of temperature showing decrease in solubility upon introduction of Al in ASR gel of compositions (a) Na/Si = 0.25 and Ca/Si = 0.11, (b) Na/Si = 0.25 and Ca/Si = 0.22, (c) Na/Si = 0.5 and Ca/Si = 0.11, (d) Na/Si = 0.5; Ca/Si = 0.22. The effect of Al on \( \log K_{sp} \) is reduced.
at higher Na and Ca contents. The temperature-dependence of log $K_{sp}$ is fitted with the equation
$log K_{sp}(T) = A_0 + A_2 T^{-1} + A_3 \ln T$ (Equation 11). The error bars are estimated from the standard deviation of triplicate measurements of elemental concentrations.

5. Solid solution model

Finally, the thermodynamic data obtained for sodium- and potassium-containing gels were compiled within the K-Si-Ca-H$_2$O and Na-Si-Ca-H$_2$O ideal solid-solution models. The solid solution models were used to predict how the chemical environments common for ASR gel [73,75] formation would affect the volume change of the ASR gel which forms. The ideal solid-solution models were created using each of the ASR gel compositions having the solubility constants ($K_{sp}$) as determined in this study. Additional thermodynamic properties comprising of Gibbs energy of formation ($\Delta G^o$), enthalpy of formation ($\Delta H^o$), entropy ($S^o$) and specific heat capacity ($C_p^o$) were determined from these studies and are summarized in Table 17. Development of the K-Si-Ca-H$_2$O and Na-Si-Ca-H$_2$O solid solution models was conducted using the GEMS3K software [132].

From the solubility studies, the concentrations of K or Na, Si and Ca in the final solutions were used to determine the thermodynamic properties of the K-Si-Ca-H$_2$O and Na-Si-Ca-H$_2$O solid solution models. The $\Delta G^o$ value of each end-member was optimized using GEMSFIT [133], which is an add-on to the GEMS3K software.

Table 17: End-member gel compositions, Gibbs energy of formation $\Delta G_f$ (kJ/mol) enthalpy of formation $\Delta H_f$ (kJ/mol) entropy ($S^o$) and specific heat capacity ($C_p^o$) of each end-member used in the K-Si-Ca-H$_2$O and Na-Si-Ca-H$_2$O solid solution models at 25°C. Sample ID nomenclature: (N or K)[x][C][y] where x and y are the molar ratios of Na$_2$O or K$_2$O, or CaO to SiO$_2$, respectively, in the ASR gel. For example: K25C1 represents (K$_2$O)$_{0.25}$ (SiO$_2$)(CaO)$_{0.11}$zH$_2$O where z is a variable composition of water.

<table>
<thead>
<tr>
<th>End-member ID</th>
<th>Chemical composition</th>
<th>$\Delta G_f$ (kJ/mol)</th>
<th>$\Delta H_f$ (kJ/mol)</th>
<th>$S$ (J/mol. K)</th>
<th>$C_p$ (J/mol. K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K0625</td>
<td>(K$<em>2$O)$</em>{0.0625}$ (SiO$_2$)(H$<em>2$O)$</em>{0.57}$</td>
<td>-1027.94</td>
<td>-1119.11</td>
<td>90.71</td>
<td>95.59</td>
</tr>
<tr>
<td>K0625C1</td>
<td>(K$<em>2$O)$</em>{0.0625}$ (CaO)$_{0.11}$ (SiO$_2$)(H$<em>2$O)$</em>{0.62}$</td>
<td>-1091.51</td>
<td>-1241.76</td>
<td>103.33</td>
<td>108.99</td>
</tr>
<tr>
<td>K0625C2</td>
<td>(K$<em>2$O)$</em>{0.0625}$ (CaO)$_{0.22}$ (SiO$_2$)(H$<em>2$O)$</em>{0.73}$</td>
<td>-1161.49</td>
<td>-1381.57</td>
<td>120.15</td>
<td>126.90</td>
</tr>
<tr>
<td>K125</td>
<td>(K$<em>2$O)$</em>{0.125}$ (SiO$_2$)(H$<em>2$O)$</em>{0.67}$</td>
<td>-1046.02</td>
<td>-1209.38</td>
<td>109.66</td>
<td>113.51</td>
</tr>
<tr>
<td>K125C1</td>
<td>(K$<em>2$O)$</em>{0.125}$ (CaO)$_{0.11}$ (SiO$_2$)(H$<em>2$O)$</em>{0.76}$</td>
<td>-1136.80</td>
<td>-1334.89</td>
<td>122.98</td>
<td>127.65</td>
</tr>
<tr>
<td>K125C2</td>
<td>(K$<em>2$O)$</em>{0.125}$ (CaO)$_{0.22}$ (SiO$_2$)(H$<em>2$O)$</em>{0.81}$</td>
<td>-1234.42</td>
<td>-1457.54</td>
<td>135.60</td>
<td>141.05</td>
</tr>
<tr>
<td>K25</td>
<td>(K$<em>2$O)$</em>{0.25}$ (SiO$_2$)(H$<em>2$O)$</em>{0.99}$</td>
<td>-1233.13</td>
<td>-1398.49</td>
<td>149.65</td>
<td>151.60</td>
</tr>
<tr>
<td>K25C1</td>
<td>(K$<em>2$O)$</em>{0.25}$ (CaO)$_{0.11}$ (SiO$_2$)(H$<em>2$O)$</em>{1.12}$</td>
<td>-1326.18</td>
<td>-1544.02</td>
<td>167.87</td>
<td>171.02</td>
</tr>
<tr>
<td>K25C2</td>
<td>(K$<em>2$O)$</em>{0.25}$ (CaO)$_{0.22}$ (SiO$_2$)(H$<em>2$O)$</em>{1.03}$</td>
<td>-1416.75</td>
<td>-1626.63</td>
<td>170.71</td>
<td>173.86</td>
</tr>
<tr>
<td>CSH-Tob-K</td>
<td>(CaO)$_{0.6667}$ (SiO$_2$)1(H$<em>2$O)$</em>{1.5}$</td>
<td>-1666.38</td>
<td>-1841.50</td>
<td>89.90</td>
<td>141.60</td>
</tr>
</tbody>
</table>

K-Si-Ca-H$_2$O solid-solution model

<table>
<thead>
<tr>
<th>End-member ID</th>
<th>Chemical composition</th>
<th>$\Delta G_f$ (kJ/mol)</th>
<th>$\Delta H_f$ (kJ/mol)</th>
<th>$S$ (J/mol. K)</th>
<th>$C_p$ (J/mol. K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N0625</td>
<td>(Na$<em>2$O)$</em>{0.0625}$ (SiO$_2$)(H$<em>2$O)$</em>{0.39}$</td>
<td>-982.33</td>
<td>-1067.77</td>
<td>76.31</td>
<td>81.34</td>
</tr>
<tr>
<td>N0625C1</td>
<td>(Na$<em>2$O)$</em>{0.0625}$ (CaO)$_{0.11}$ (SiO$_2$)(H$<em>2$O)$</em>{0.55}$</td>
<td>-1069.03</td>
<td>-1221.88</td>
<td>96.63</td>
<td>103.03</td>
</tr>
</tbody>
</table>

Na-Si-Ca-H$_2$O solid solution
<table>
<thead>
<tr>
<th>Sample</th>
<th>Formula</th>
<th>K concentration</th>
<th>Si concentration</th>
<th>Ca concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>N0625C2</td>
<td>(Na₂O)₀.₀₆₂₅(CaO)₀.₂₂(SiO₂)(H₂O)₀.₆₄</td>
<td>-1163.71</td>
<td>-1355.97</td>
<td>112.05</td>
</tr>
<tr>
<td>N125</td>
<td>(Na₂O)₀.₁₂₅(SiO₂)(H₂O)₀.₄₉</td>
<td>-1033.69</td>
<td>-1149.59</td>
<td>91.35</td>
</tr>
<tr>
<td>N125C1</td>
<td>(Na₂O)₀.₁₂₅(CaO)₀.₁₁(SiO₂)(H₂O)₀.₆₃</td>
<td>-1127.20</td>
<td>-1297.98</td>
<td>110.27</td>
</tr>
<tr>
<td>N125C2</td>
<td>(Na₂O)₀.₁₂₅(CaO)₀.₂₂(SiO₂)(H₂O)₀.₇₂</td>
<td>-1182.91</td>
<td>-1432.07</td>
<td>125.69</td>
</tr>
<tr>
<td>N25</td>
<td>(Na₂O)₀.₁₂₅(SiO₂)(H₂O)₁.₂₂</td>
<td>-1286.54</td>
<td>-1464.82</td>
<td>158.48</td>
</tr>
<tr>
<td>N25C1</td>
<td>(Na₂O)₀.₂₅(CaO)₀.₁₁(SiO₂)(H₂O)₁.₁₄</td>
<td>-1325.74</td>
<td>-1550.29</td>
<td>162.02</td>
</tr>
<tr>
<td>N25C2</td>
<td>(Na₂O)₀.₂₅(CaO)₀.₂₂(SiO₂)(H₂O)₁.₀₈</td>
<td>-1398.09</td>
<td>-1641.48</td>
<td>166.95</td>
</tr>
<tr>
<td>CSH-Tob-Na</td>
<td>(CaO)₀.₆₆₆₆(SiO₂)(H₂O)₁.₅</td>
<td>-1665.37</td>
<td>-1841.50</td>
<td>89.90</td>
</tr>
</tbody>
</table>

Figure 33 shows good agreement of the K-Si-Ca-H₂O solid solution model with the experimental results. The calculated values for the concentrations of K, Si, and Ca in solution are within an order of magnitude of the measured values. The prediction of the Ca values was the least accurate. The optimization method used a sum of square errors minimization approach which is affected by larger differences between the calculated and measured values. Figure 34 shows good agreement of the Na-Si-Ca-H₂O solid solution model with the experimental results. The calculated aqueous concentrations of Na, Si, and Ca are within an order of magnitude of the measured values. Further, the solid solution models performed well at the different temperatures as shown in Figures 33 and 34. The calculated concentrations of K or Na, Si and Ca are within an order of magnitude of the measured values using the K-Si-Ca-H₂O and Na-Si-Ca-H₂O models at 5°C, 25°C, and 45°C.

**Figure 33:** Comparison of K-Si-Ca-H₂O solid solution model with solubility studies considering the elements in solution (a) K, (b) Si, and (c) Ca. The solubility studies were conducted at temperatures of 5°C (white triangles), 25°C (red squares) and 45°C (blue diamonds). The solubility studies tested ASR gels with K/Si=0.125–0.5 and Ca/Si=0–0.22.
To simulate the volume change of ASR gels in different chemical environments, GEMS-based calculations for the following system was carried out: 1 g of SiO$_2$ + M$_2$O + CaO in 30 mL of water with varying molar ratios of 0<M/Si<0.5 (where M is Na or K) and 0 < Ca/Si < 0.22 at temperatures of 5°C, 25°C and 45°C. The results of the simulations for the K-Si-Ca-H$_2$O and Na-Si-Ca-H$_2$O systems are shown in Figure 35 and Figure 36, respectively. For instance, the largest volume of ASR gel formed in the K-Si-Ca-H$_2$O system was observed at K/Si = 0.1 and Ca/Si = 0.22 at 5°C (Figure 35a), analogous to observations in the Na-Si-Ca-H$_2$O system (Figure 36a); the volume of ASR gel formed was consistently lower in the latter. Higher Ca/Si ratios produced larger volumes of ASR gel because of the tendency of Ca to precipitate out of solution to form calcium-silicate hydrates. In general, the greatest volumes of ASR gels for a given composition are observed at the lowest temperature investigated, 5°C.

In all the simulations (K- and Na-containing), solid amorphous silica was observed in the solid phase assemblage at high Si (i.e., prior to the occurrence of a maximum in gel volume in Figures 35 and 36). The molar ratio of M/Si where all the silica has dissolved and formed the ASR gel varies for each of the compositions and temperatures. For instance, in the K-Si-Ca-H$_2$O system with a Ca/Si = 0.11 at 25°C, no more solid silica was observed in the simulation results at K/Si = 0.15 and at K/Si ≥ 0.2, the volume of ASR gel decreased. This was due to greater levels of Si dissolved into solution at high pH instead of precipitation to form the ASR gel. The solution compositions at which silica is completely dissolved, Ca/Si, the presence of either Na or K, and temperature were the key factors that affected the maximum volume of the ASR gel. Therefore, to reduce the volume of ASR gel, an environment having low Ca and high Na contents is relatively optimal based on the simulation results.
Figure 35: Volume of K-Si-Ca-H$_2$O ASR gel formed at varying molar ratios of $0 < \text{K/Si} < 0.5$ and $0 < \text{Ca/Si} < 0.22$ at temperatures of (a) 5°C, (b) 25°C, and (c) 45°C.

Figure 36: Volume of Na-Si-Ca-H$_2$O ASR gel formed at varying molar ratios of $0 < \text{Na/Si} < 0.5$ and $0 < \text{Ca/Si} < 0.22$ at temperatures of (a) 5°C, (b) 25°C and (c) 45°C.

6. Summary

This report presents the first comprehensive study establishing the thermodynamic properties of end-member compositions of alkali-silica reaction gels. These phases are thought to exhibit similar characteristics (e.g., low density and expansiveness) to amorphous siliceous phases that form during neutron irradiation of silicates (e.g., quartz), analogous to the manifestations in a nuclear power plant (NPP) concrete exposed to neutron radiation. [134]

The results indicate that the thermodynamic properties of ASR gels particularly its solubility as expressed by $\log K_{sp}$ is influenced by both its composition and the aqueous exposure temperature. The $\log K_{sp}$ of Na-based gels varies more substantially with gel composition, compared to the K-based variants. This observation can be explained, partly, by the higher effective charge of hydrated K$^+$ ions than Na$^+$ ions producing stronger bonds with the non-bridging oxygens in the silicate framework, and thereby resisting ion exchange as opposed to Na$^+$ ions, which are weakly bonded and more readily exchange with Ca to form less soluble gels. The established $\log K_{sp}$ values also increase with increasing temperature; greater enhancements are observed at higher alkali and Ca contents. The presence of Al in the gel was shown to result in a reduced solubility, with the largest reductions in magnitudes observed at lower temperatures and Na and Ca contents.
The expansion properties of ASR gels are widely reported to depend on the composition (i.e., Ca/Si, Na/Si, and K/Si). [135] Because the compositions of field ASR gels vary widely, it can be implied that not all gel compositions are necessarily deleterious. For an ASR gel to be deleterious, it needs to have the capacity to both swell extensively and exert and maintain pressure to its surroundings while swelling. [75,135] Equipped with the thermodynamic data obtained in the course of this project, mitigation systems can be engineered to suppress ASR-induced damage in concretes by way of altering system compositions. For instance, the characteristics of the ‘aggregate–pore solution’ interface (e.g., composition and the evolution of aqueous speciation in response to pH and temperature gradients) can be tuned to prevent ASR gel precipitation, or to favor the formation of less expansive gels. A full description of the thermodynamic model for ASR gels would require further studies on sublattice solid solution models and the composition-structure-solubility relationships of ASR gels.
Milestone/Task 4
Reactive-Transport simulation of expansive product formation in virtual microstructures

1. Objectives
This milestone aims to develop a finite element framework to quantify damage in cementitious material undergoing degradation due to aggregate expansion. Expansion resulting from reactive transport is simulated using thermal strains.

2. Simulation Approach
As mentioned earlier, the expansion of aggregates because of reactive transport is simulated using thermal strains. We use the aggregate properties (such as the coefficient of thermal expansion) and an imposed temperature to introduce expansive strains. Thus, here, the influence of various expansive aggregates on stress-development is investigated. The materials properties for the three different expansive aggregates investigated, along with that of the hydrated cement paste (HCP) are shown in Table 13.

<table>
<thead>
<tr>
<th>Material parameters</th>
<th>Acetal</th>
<th>High Density Polyethylene (HDPE)</th>
<th>Polypropylene (PP)</th>
<th>HCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus (GPa)</td>
<td>2</td>
<td>1.2</td>
<td>1.3</td>
<td>20</td>
</tr>
<tr>
<td>Coefficient of thermal expansion ((10^6 \mu\varepsilon/\mu\varepsilon\cdot\degree C))</td>
<td>110</td>
<td>150</td>
<td>200</td>
<td>20</td>
</tr>
</tbody>
</table>

Stress analysis was carried out while increasing the temperature to evaluate relative performance of different expansive aggregates during temperature-induced damage in hardened cement paste. A finite element (FE)-based stress analysis framework [136] was initially employed. This report details the finite element analysis in the commercial package ABAQUS, but efforts are ongoing to implement aggregate expansion induced cracking in the MOOSE framework, using the experimental data obtained in the previous tasks of this project. The framework is broadly similar, whether implemented in ABAQUS or MOOSE, and consists of the following components:

2.1 Generation of representative volume element (RVE)
Generation of RVE is accomplished using the Lubachhevsky-Stillinger algorithm. [137-139] This algorithm employs a hard contact model and hence particle overlaps are not allowed. Here, the RVE is set to be a cube. First, the desired number of particles (aggregates) is randomly distributed inside the periodic bounding box with random initial velocities of the particles. The radius of each particle is initialized as zero. The radius of the \(i\)th particle \(r_i\) in the next event is a function of the growth rate \(g_i\), which is tailored to attain the desired particle size distribution shown in Equation 18.

\[
\frac{dr_i}{dt} = g_i
\]  

(18)

Here \(i = 1, 2, \ldots\) is the number of particles. The growth rate between time \(t^n\) and \(t^{n+1}\) is computed using a finite difference scheme as follows:
The particle radii are then updated as follows for time $t^{n+1}$ by employing the growth rate and time increment ($\Delta t$) as:

$$ r_i^{n+1} = r_i^n + g_i \Delta t $$

(20)

In addition, the position of particle ‘$i$’ at time $t^{n+1}$ is updated considering a constant velocity ($v_i^n$) between the time nodes:

$$ x_i^{n+1} = x_i^n + v_i^n \Delta t $$

(21)

The vector that connects the centers of particles ‘$i$’ and ‘$j$’ is obtained by subtracting the position vectors of the two particles:

$$ I_{ij}^{n+1} = x_j^{n+1} - x_i^{n+1} $$

(22)

The particles ‘$i$’ and ‘$j$’ are expected to be in contact if the sum of their radii is equal to the length of the connection vector. The time step size can be calculated as:

$$ \Delta t = \min \left[ -V \pm \sqrt{V^2 - UW} \right] $$

(23)

where $\Delta t > 0$ and $V$, $U$ and $W$ are given as:

$$ V = I_{ij}^n \left[ v_j^n - v_i^n \right] - [r_i^n + r_j^n] [g_i + g_j] $$

(24a)

$$ U = [v_j^n - v_i^n]^2 - [g_i + g_j]^2 $$

(24b)

$$ W = [I_{ij}^n]^2 - [r_i^n + r_j^n]^2 $$

(24c)

The time step calculation (Equation 23) is performed for each particle pair that is able to collide and thus a minimum time step for all the possible collisions is adopted to move forward for the next event. All the particle positions $x_i^{n+1}$ are updated using the forward Euler scheme (Equation 21) and a new search for the next collision(s) is started. The post-contact velocities are computed as follows:

$$ v_i^{n+1} = \min \{v_i^{n+1}, v_j^{n+1}\} - g_i, \quad v_j^{n+1} = \max \{v_i^{n+1}, v_j^{n+1}\} + g_i $$

(25)

Thus, all the above-mentioned steps are repeated and in the process of iterations the particles change position in the bounding box, collide, and grow in order to obtain the desired volume fraction. Finally, the obtained microstructural information is implemented via a Python language script to enable it to be imported to a finite element modeling software such as ABAQUS™.

### 2.2 Boundary condition

Choosing appropriate microscopic boundary conditions is an essential step in any numerical stress analysis procedure. In micromechanics, the commonly adopted boundary conditions are: essential boundary conditions, where uniform displacements are applied at the boundaries, or Neumann boundary conditions, where uniform tractions are prescribed at the boundaries of the unit cell. These boundary conditions have been applied to predict effective properties of several materials including cementitious binders. Since it is difficult to realize uniform boundary conditions in experimental setups, mixed boundary conditions are also proposed. In this work, periodic boundary conditions (PBCs) are adopted since they provide better...
approximations of effective properties of heterogeneous materials even with relatively smaller RVEs that are favorable for computational expediency. PBCs ensure two continuity criteria at the boundaries of neighboring unit cells in order to ensure assembly of individual unit cells as a physical continuous body: [145] (i) displacement continuity, i.e., neighboring unit cells cannot be separated or they cannot penetrate each other; and (ii) traction continuity at the boundary of neighboring unit cells. The displacement field in any 2D periodic microstructure is given as:

\[ v_i(x_1, x_2) = \varepsilon^0_{ij} x_j + v^*_i(x_1, x_2) \]  

(26)

Here, \( \varepsilon^0_{ij} \) is the applied strain tensor, and \( v^*_i \) is a periodic function representing the modification of linear displacement field due to the heterogeneous microstructure. Figure 37 shows a schematic representation of periodic boundary conditions. For the unit cell shown in Figure 37b, the displacements on a pair of parallel opposite boundary edges are given as:

\[ v^{s+}_i = \varepsilon^0_{ij} x^{s+}_j + v^*_i \]  

(27a)

\[ v^{s-}_i = \varepsilon^0_{ij} x^{s-}_j + v^*_i \]  

(27b)

Here, \( s^+ \) and \( s^- \) are the \( s^{th} \) pair of two opposite parallel boundary surfaces of the unit cell. The periodic function \( v^* \) is the same at both parallel opposite edges due to periodicity. The difference between the displacement fields of the two opposite parallel boundary edges is given as:

\[ v^{s+}_i - v^{s-}_i = \varepsilon^0_{ij} (x^{s+}_j - x^{s-}_j) = \varepsilon^0_{ij} \Delta x_j \]  

(28)

For a pair of opposite parallel boundary edges, \( \Delta x_j \) is constant for a specified \( \varepsilon^0_{ij} \). The perturbation is introduced into the system of equations through a reference node which acts only as a carrier for the load and is not attached to any element in the model. The general form of a complete set of equations can be written as:

\[ v^{s+}_i - v^{s-}_i + v^{\text{dummy}}_i = 0 \]  

(29)

2.3 Finite element simulation

The RVE is meshed using the Python script and the analysis is implemented via a FE solver. To efficiently handle post-processing of the simulated individual element stresses, a homogenization module is implemented to obtain effective volume-averaged RVE stresses and strains. The post-processing module contains a MATLAB subroutine that operates on the data file generated by ABAQUS\textsuperscript{TM} containing elemental volumes, average stresses/strains, and yields volume-averaged stresses/strains (see overview in Figure 37).
First the relative influences of different expansive aggregates were evaluated by a single inclusion model (5% by volume). The temperature was monotonically increased in 15°C increments. Figure 38 shows the stress distributions in the microstructure. The maximum principal stress exceeds 3 MPa for all the aggregates. Hence, the simulation suggests that all the aggregates will initiate damage with a 15°C temperature increase (assuming a tensile strength of around 3 MPa for the HCP).

Next, the effects of multiple inclusions with random distribution in the microstructure were studied. Figure 39 shows comparisons of single and multiple-inclusion cases for Acetal aggregates. Both the microstructures contain 5% inclusion by volume. A representative area of size 2.4 mm × 2.4 mm is chosen for the single inclusion case whereas a size of 10 mm × 10 mm is chosen for multiple inclusion case. The inclusion size is fixed (0.6 mm) for both the cases. The multiple inclusion case shows higher stresses due to the close proximity of inclusions in the microstructure. Hence, in reality, the maximum principal stresses will be higher than that shown for single inclusion cases in Figure 38.
To investigate the influence of expansive aggregate on the damage behavior, a framework similar to that presented in Figure 37 is used. Temperature-induced damage in HCP was simulated using the extended finite element method (XFEM). XFEM is an extension of the conventional FEM where local enrichment functions are incorporated in the finite element approximation. XFEM ensures the presence of discontinuities through special enriched functions with additional degrees of freedom (see Task 5 Report for more details on XFEM). Thus, XFEM simulates path-independent crack initiation and propagation based on the damage criteria provided. A maximum principal stress-based damage initiation criterion is used and a bilinear traction-separation law describes crack propagation. The XFEM simulation results for varying temperature increases are shown in Figure 40. The data suggest that a temperature increase of 15°C is sufficient to cause damage in the microstructure when using 5% of HDPE aggregates by volume. In the XFEM environment, higher aggregate volume fractions could not be used because of stability and convergence issues. This is another motivation to use a MOOSE-based simulation, as is being implemented currently for several microstructures.

To evaluate the effect of homogenized material properties, a restrained ring test is simulated using conventional FE analysis. A two-dimensional plane stress FE model is used to characterize and compute the mechanical response of the HCP ring subjected to temperature change. A plane strain model is used since the thickness of the cement paste in the $z$-direction is comparable to the thickness in the radial direction. Using symmetry boundary conditions, a one-quarter section of the ring is subjected to temperature cycles (see Figure 41). Figure 42 shows the stress distributions (maximum principal stress) at different temperatures during the first temperature cycle (25°C, 45°C, 5°C, 45°C) in the HCP. When the temperature is increased from 25°C to 45°C the maximum principal stress (tensile) reaches 0.7 MPa. When the temperature is decreased from 45°C to 5°C, a compressive stress of 6.9 MPa is developed. The ring again shows a tensile stress of 0.7 MPa when
heated from 5°C to 45°C. When homogenized properties for the HCP-HDPE system are used, the maximum tensile stress increases to 0.87 MPa when heated to 45°C, as shown in Figure 43. A simple rule of mixtures is used to obtain effective material properties for the HCP-HDPE system.

**Figure 41:** An illustration of the FE-model showing the essential boundary conditions for the quarter-ring model and the FE-mesh used for extended finite element analysis.

**Figure 42:** Principal stress distributions in the HCP ring at different temperatures in the first temperature cycle (25°C, 45°C, 5°C, 45°C). The confining invar rings are not shown.

Figure 44 shows the applied temperature cycle and the simulated stress responses for HCP and HCP-HDPE system. Both tensile and compressive stresses increase when HDPE aggregates are incorporated in cement paste matrix. The simulated stress values for the HCP-HDPE composite correlate well with the experimental values for the first cycle. After the first cycle, however, it appears as though the outer invar ring might have lost contact with the material surface and this results in a reduction in the compressive stresses. It should be noted that the maximum principal stress (tensile), simulated using the homogenized material properties, is significantly lower as compared to the microstructural stress analysis (Figures 41-42). While, the maximum principal stress in the microstructure is higher due to heterogeneity and incompatibility in stiffness and coefficient of thermal expansion between the aggregates and the matrix, the same effect is absent in case of the simulation since the material is modeled using homogeneous effective properties. The homogenized model is required to overcome the instability effects associated with XFEM. Under the applied temperature cycle, the micro-cracks appear in the microstructure although the effect is not visible at the structure-level. The instabilities associated with XFEM resulted in the use of a continuum framework in MOOSE as described in the Task 5 report.
3. Microstructure-based damage modeling in MOOSE

A mesoscale microstructure framework is implemented in MOOSE to simulate the expansion and corresponding damage propagation under thermal and irradiation-induced swelling of otherwise elastic aggregates. The framework shown schematically in Figure 45, will be validated with the experimental results of Maruyama et al., [146] which to date feature the most comprehensive set of tests on irradiated concrete. The framework considers the effect of elevated temperature and high neutron fluence on the mortar and aggregate separately. The presence of high neutron fluence level causes amorphization and radiation-induced volume changes in the aggregates which are much larger than those observed during the thermal expansion or alkali silica reactions. [147] The elevated temperature also has a healing effect [148] that reduces the expansion and is considered in this framework. At elevated temperatures, gamma irradiation also causes drying shrinkage in the paste due to the loss of water. Using the gas measurements and the water vapor sorption isotherms, the magnitude of drying shrinkage is estimated. Although, the effect of
radiation on creep is not well understood, the effect of elevated temperature and humidity on creep is well-known and is considered in the present framework.

3.1 Microstructure, mesh generation, analysis type and boundary condition

The microstructure has been generated based on the particle size distribution of the coarse aggregates provided by Maruyama et al. [146] The particle size distribution of sand has not been given. Moreover, it is very difficult to include the sand particles in the simulation due to their small sizes. Hence, the property of cement paste was upscaled to mortar and used in the simulation. Meshing has been carried out in CUBIT [149] using QUAD4 elements. Due to the symmetrical nature of the specimen about the center axis, a 2D axisymmetric simulation was carried out toward understanding of the particle matrix interaction and the degradation mechanism. The boundary conditions are as per axisymmetric approximation and shown in Figure 45.

![Figure 45: Mesoscale microstructure-based FE framework to detect damage in concrete with expansive aggregates.](image)

3.2 Material properties

3.2.1 Aggregate

The aggregate is treated as a linear elastic material undergoing radiation-induced volumetric expansion. The dynamic modulus of the aggregate (called as GA in the paper) is given as 65 GPa with a Poisson ratio of 0.28. [146] As the static modulus is observed to be lower than the dynamic modulus by about 10%, [150] we have taken the static modulus as 58.5 GPa. The modulus further reduces under neutron irradiation due to degradation. However, no measurements of decrease of elastic modulus due to neutron irradiation were carried out. Elleuch et al. [151] carried out the experiments on serpentine aggregates and found that the pulse velocity reduces from 7200 m/sec to 4750 m/sec from 1 to 10 (10^{19} n/cm^2). This means that the elastic modulus reduces to 56% of the original value (elastic modulus proportional to square of the pulse velocity). In our simulations, we have used the same trend so that the elastic modulus reduces from 58.5 GPa to 25.65 GPa (see Figure 46). The Poisson’s ratio is best estimated from dynamic measurements; [150] hence the value of 0.28 is taken.
3.2.2 Motor

The mortar has been modeled as a quasibrittle elastic material undergoing stiffness degradation and long-term creep owing to the elevated temperature. The cement mortar is modeled as an elastic material \((E_m=30.25 \text{ GPa}, \nu=0.2)\) undergoing drying shrinkage, thermal deformation and creep owing to the high temperature \((T\sim70^\circ\text{C})\). The young modulus is back calculated based on the modulus of concrete \((E_c=37.5 \text{ GPa})\) based on the following empirical relation, \([152]\)

\[
\frac{1}{E_c} = \frac{c}{E_a} + \frac{1-c}{E_m}
\]  

where, \(E_c\), \(E_a\) and \(E_m\) are the modulus of concrete, aggregate and mortar respectively. \(c\) is the volume fraction of the aggregate (taken as 0.4). \([146]\)

3.2.2.1 Creep

There is no data in open literature regarding creep under neutron irradiation hence its effect will be ignored in the present simulation. However, the effect of humidity and temperature will be considered here. \([153]\) A single Kelvin Voigt chain with an additional dashpot is used to model recoverable and non-recoverable creep as was done in a previous study. \([153]\) The effect of elevated temperature on creep is considered using Arrhenius law, such that the Kelvin-Voigt characteristic time is given by:

\[
\tau_p(T) = \exp[T_{act} \left( \frac{1}{T} - \frac{1}{T_0} \right)]\tau_p(T = T_0)
\]  

where, \(T_{act}\) is the activation temperature for creep \((5000\text{K})\). \([154]\) \(\tau_p\) is the characteristic time of the specimen and is taken as 2 days. \([155]\) The viscosity tensor for the Kelvin Voigt model is calculated by considering the viscosity in terms of relative humidity 'h' as,

\[
\eta_p(h) = \left[ \left( \frac{1-h}{h_c} + \exp \left( \frac{1-h}{h_c} \right) \right) \right] \eta_p(h = 1)
\]  

where, \(h_c\) is a material property equal to 0.2. \([153]\) \(\eta_p\) is taken as 40 GPa.d. \([153]\)

3.2.2.2 Post Peak Response

The smeared crack model is used in this approach because of the flexibility with which the damage behavior can be simulated by specifying the ultimate tensile strain at the end of softening curve. The existing smeared cracking code in MOOSE consisted of specifying the tension

\[\text{Figure 46: Variation of elastic modulus of aggregate with fluence.}\]
softening law. This has been known to cause mesh sensitivity in the results. [156] This requires specifying the fracture energy, $G_F$ as a material parameter. If the fracture energy is known, then the fracture strain for each element is computed as:

$$
\varepsilon_f = \frac{2G_F}{\sigma_{cr} l}
$$

(33)

where $\sigma_{cr}$ is the cracking stress and $l$ is the characteristic length for each element given as the square root of the area of each element. In this study, a constant strength of 4 MPa [146] is adopted for the mortar as the strength (cracking stress) of a cementitious material does not depend on strain rate for very low values. [157] The fracture energy is taken as 0.026 N/m. [158]

3.3 Loading
3.3.1 Aggregate

3.3.1.1 Radiation induced Volumetric Expansion

It has been observed that aggregates with covalent bonds (siliceous aggregates) are more susceptible to radiation induced expansion than aggregates with ionic bonds. [147] Quartz, which is present in aggregates is more susceptible to irradiation-induced swelling, however, no direct correlation could be obtained between quartz content and degree of expansion suggesting factors including other minerals, texture, and grain boundaries influencing the rate of expansion. [146] As these effects are difficult to be considered at this stage, we will consider uniform volumetric expansion of aggregates. It is to be noted that temperature also affects the degree of quartz metamictization (Bykov et al.). [148] Bykov et al. [148] found that expansion decreases with increasing temperature indicating that thermal heating heals the damage in the aggregate. They considered the thermal healing at high temperature and expressed RIVE using the nucleation and growth model as,

$$
\varepsilon_a = \varepsilon_{max} \left( 1 - \exp \left( \frac{n}{K(T)} d \right)^{d/T} \right)
$$

(34)

where, $\varepsilon_{max}$ is the maximum expansion volume as observed in experiments (0.18 in this case), [146] $n$ is the fast neutron fluence (n/cm$^2$), $K(T)$ is the fast neutron fluence when expansion reaches half the maximum expansion volume (n/cm$^2$), $T$ is the temperature (in Kelvin), $d$ is the dimension coefficient taken as 2.38 based on Field et al. [159] $K(T)$ is given by, [146]

$$
K(T) = 0.45 \times 10^{2.0} \times \frac{\exp(2000/298)}{\exp(2000/T)}
$$

(35)

The thermal deformation which is negligible in comparison to RIVE is ignored in the present simulations. Moreover, elevated temperature causes healing and thus controls RIVE as considered in this study.

3.3.2 Mortar
3.3.2.1 Drying Shrinkage

The linear drying shrinkage of cementitious materials can be directly related to the pore water content or the internal pore relative humidity of the specimen. [160,161]

$$
\varepsilon_{ld}(t) = \varepsilon_{SH,\infty}(1 - H(x, t))
$$

(36)
where, $\varepsilon_{SH,\infty}$ is the free shrinkage coefficient (taken as 0.0015) [146] which is equal to the maximum shrinkage obtained at infinite time. $H(x, t)$ is the internal humidity at the depth ‘$x$’ from the surface of specimen at time ‘$t$’ given by:

$$H(x, t) = H_I - (H_I - H_S)erfc\left(\frac{x}{2\sqrt{D_Mt}}\right)$$

where, $H_I$ is the internal relative humidity of a sealed specimen, $H_S$ is the relative humidity at the surface. $D_M$ is the moisture diffusion coefficient. From the heating test, it was observed that the high temperature induces evaporation of water and that equilibrium is reached inside the capsule. However, the humidity gauge tank in the experiments reported in Maruyama et al. [146] showed the same absolute humidity level, which was much less than the saturated level as seen during the irradiation tests. This indicates insufficient drying solely due to the heating process. Thus, irradiation, which causes radiolysis of water, is likely the main reason for the water loss. This means the effect of moisture gradient inside the specimen could be ignored in the present simulations. A future modification to the simulation scheme will explicitly consider the validity of this assumption but currently, there is no established method to discriminate between radiolysis and evaporation-induced moisture loss. Gas is also emitted due to radiolysis and it builds the pressure inside the capsule, which is released once the pressure reached 1.25 bar. To find the change in the internal relative humidity, we use the water vapor desorption isotherm (WVSI) obtained by Maruyama et al. [146] From the WVSI’s, the humidity level corresponding to each pore water content is known. During the irradiation test, the water evaporated is measured continuously and the total water content is also known, thus the pore water content could be estimated (shown in Figure 47a) which will give the internal RH from the WVSI. The drying shrinkage is shown in Figure 47b.

![Figure 47: Variation of (a) water content and (b) internal RH with fluence.](image)

4. Result

Figure 48 compares the calculated and measured displacements at the top of the specimen, showing that the simulation underestimates the response at later ages. It was realized that the fixed smeared cracking code in MOOSE makes the material orthotropic once cracking initiates. This violates the isotropic condition of Kelvin Voigt model. Therefore, the creep model never runs, and thus the material does not exhibit any relaxation as well. This indicates a high amount of damage
in the material which is evident from Figure 49. However, the results of FE simulations clearly show that stress concentrates around the aggregates in the mortar, and that microstructural damage is distributed throughout the entire specimen. An isotropic damage model is required for the present simulation which can be coupled with the viscoelastic code in MOOSE framework to obtain accurate predictions of coupled creep damage behavior. One of such models being currently implemented in MOOSE is given as, [152]

$$\sigma = (1 - d) \cdot E \cdot \varepsilon$$

(38)

where, $\sigma, E, \varepsilon$ are the stress, elasticity and strain tensor respectively. ‘$d$’ is the scalar isotropic damage variable.

5. Summary

An extended finite element (XFEM) framework was implemented to determine the extent of expansion-related cracking in cementitious materials. Thermal strains were used to simulate microstructural expansion. Three different expansive aggregates were used, either as single
inclusions, or as multiple inclusions in a microstructure to simulate damage. XFEM framework could not capture the effects of higher volume fraction of aggregates due to convergence issues. A conventional FE model of a restrained ring test using homogenized properties of the cement paste and expansive aggregate phases was used to evaluate damage under imposed thermal strains. A microstructural model is being implemented in the MOOSE environment, which accounts for thermal, creep, and neutron fluence-induced damage in aggregates and mortar. The model requires isotropic damage model which can be coupled with the creep model to accurately predict the coupled creep and damage behavior in the microstructure. The restrained ring model developed in MOOSE (see Task 5 report) facilitates the implementation of this coupled expansion and damage model, which will be validated using experimental results.
Milestone/Task 5
X-FEM modeling of damage evolution due to expansive phase formation

1. Objectives
This milestone aims to develop a finite element (FE) framework to quantify damage in cementitious material undergoing degradation due to aggregate expansion. In the first part of the report, microstructure-based XFEM used in Task 4 is implemented in a mesoscale continuum structure (beam) to evaluate the crack propagation process, whereas in the second part, MOOSE implementation of a continuum damage framework is reported for cementitious systems undergoing volume change. The volume change formulations and MOOSE implementation are carried out for restrained ring specimens containing compliant or stiff inclusions. In the final validation task, this framework will be used along with expansion data from experiments to simulate cracking and predict damage evolution in mesoscale (centimeter sizes) specimens.

2. Part I: X-FEM for crack propagation in a meso-scale structure (a beam)
XFEM was initially proposed to be used to detect damage in cementitious materials undergoing radiation-induced deleterious expansions. The disadvantages of using XFEM pertaining to this work were: (i) the need to obtain the concrete damage plasticity (CDP) models for inputs into the model to be used in a finite element analysis package such as ABAQUS™, and (ii) the fact that XFEM was not implemented in the MOOSE framework developed at Idaho National Laboratories for coupled multiphysics problems, at the time of doing this work. Hence, we use XFEM in this section (using ABAQUS™) to demonstrate the applicability of this framework for understanding crack propagation under mechanical loading, which can be extended easily to thermal or expansion-induced loading. We also leave open the potential to introduce this to MOOSE, once the XFEM is incorporated into MOOSE. Note that, a mortar microstructure (see Task 4 section) is homogenized in utilizing XFEM.

2.1 Simulation approach
In the XFEM framework, the displacement field consists of two parts – one is continuous and the other is discontinuous. The former is the standard displacement field corresponding to an uncracked situation. Local enrichment functions are incorporated in the FE approximation in order to model the crack (discontinuities) in an efficient manner. The enriched functions have additional degrees of freedom and simulate path-independent crack initiation and propagation based on the damage criteria provided. [163] The asymptotic crack tip functions \( F_\alpha \) are given as:
\[
F_\alpha (x) = \left[ \sqrt{r} \sin \frac{\theta}{2}, \sqrt{r} \cos \frac{\theta}{2}, \sqrt{r} \sin \frac{\theta}{2} \sin \frac{\theta}{2}, \sqrt{r} \sin \frac{\theta}{2} \cos \frac{\theta}{2} \right]
\]  
where the crack tip is at the origin of the polar coordinate system and \( \theta = 0 \) is tangent to the crack tip. The XFEM damage model requires appropriate damage initiation criteria. The maximum principal stress criterion is adopted in this study and the crack is considered to be initiated if the maximum principal stress exceeds the tensile strength of the mortar. A bilinear traction-separation law [164] is used for damage propagation, as shown below. The fracture energy \( (G_F) \) is the area under the entire traction-separation curve, given as:
\[
G_F = \int_0^\infty f(w) dw
\]
\[
f(w) = \begin{cases} f_t - (f_t - f_1) \frac{w}{w_1} & \text{for } w \leq w_1 \\ f_1 - f_1 \frac{(w - w_1)}{(w_c - w_1)} & \text{for } w_1 > w \end{cases}
\]

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where $f_t$ is the tensile strength of the material, $w_c$ is the critical crack tip opening displacement, and $f_i$ and $w_i$ are the stress and opening displacement corresponding to the kink in the bilinear traction-separation curve.

The numerical simulation framework incorporates the concrete damage plasticity (CDP) model [165,166] beyond the linear elastic regime for fracture simulation. CDP is a material model based on a combination of damage and plasticity theory. The plasticity theory is used to describe both the compressive and tensile responses of concrete, whereas the damage theory is used for the cyclic and unloading characteristics. In this model, isotropic damage is represented as:

$$
\sigma = (1 - d) D_0^{el} : (\varepsilon - \varepsilon^{pl}) = D^{el} : (\varepsilon - \varepsilon^{pl})
$$

(41)

where $\sigma$ is the Cauchy stress tensor, $d$ is the scalar stiffness degradation variable, $\varepsilon$ is the strain tensor, $\varepsilon^{pl}$ is the plastic strain, $D_0^{el}$ is the initial elastic stiffness of the material, and $D^{el}$ is the degraded elastic stiffness tensor. The effective stress tensor $\bar{\sigma}$ is given as:

$$
\bar{\sigma} = D_0^{el} : (\varepsilon - \varepsilon^{pl})
$$

(42)

Damage states in tension and compression are characterized independently by two hardening variables which are the equivalent plastic strains in compression and tension respectively. The plastic flow is given as:

$$
\dot{\varepsilon}^{pl} = \frac{1}{\lambda} \frac{\partial G(\bar{\sigma})}{\partial \bar{\sigma}}
$$

(43)

where, the flow potential, $G$ is given using a Drucker-Prager hyperbolic function as:

$$
G = \sqrt{(f_c - m \cdot f_t \cdot \tan \beta)^2 + q^2 - \bar{p} \cdot \tan \beta - \sigma}
$$

(44)

Here, $f_t$ is the tensile strength and $f_c$ is the compressive strength, $\beta$ is the dilation angle and $m$ is the eccentricity of the plastic potential surface, $\bar{p}$ is the effective hydrostatic stress and $q$ is the Mises equivalent effective stress. The CDP model uses a yield condition based on loading function:

$$
F = \frac{1}{1 - \alpha} (q - 3.\alpha \cdot p + \theta(\varepsilon^{pl})(\sigma_{max}^c) - \gamma(-\sigma_{max}^c)) - \sigma_{max}^t (\varepsilon^{pl})
$$

(45)

where the function $\theta(\varepsilon^{pl})$ is given as:

$$
\theta(\varepsilon^{pl}) = \frac{\bar{\sigma}_c (\varepsilon^{pl})}{\bar{\sigma}_t (\varepsilon^{pl})} (1 - \alpha) - (1 + \alpha)
$$

(46)

The parameter $\alpha$ , which is based on the ratio of biaxial compressive strength ($f_{iso}$) to uniaxial compressive strength ($f_c$), is defined as:

$$
\alpha = \frac{(f_{iso}/f_c) - 1}{2(f_{iso}/f_c) - 1}
$$

(47)

2.2 Numerical Simulation of Three Point Bending Test for Mortar Beams using XFEM in ABAQUS

A 2D XFEM model is used to simulate three-point bending of a notched mortar beam. The beam has a span of 100 mm, and a cross section of 25 mm × 25 mm. For experimental evaluation of fracture behavior, four replicate beams were tested. The notch depth was 19 mm (corresponding to a notch depth-to-beam depth ratio of 0.25). The beams were tested in a CMOD-controlled mode during the loading cycles and in a load-controlled mode during the unloading cycles. [167] The meshed beam model is shown in Figure 50.
The beam has an initial notch, which is 1 mm wide and 3.75 mm deep, at the mid-span. The two pin supports and the loading head at the top are defined as rigid bodies. The displacement is applied at a reference point tied to the loading head. Traction-separation behavior is quantified using data on the cement mortar made using the same materials and proportions, reported in an earlier publication. [168] The values for the concrete damage plasticity (CDP) variables, i.e., $\beta$ which is the dilation angle at high confining pressure, $m$ which is the eccentricity of the plastic potential surface, $\gamma$ which is the parameter that determines the shape of the loading surface in the deviatoric plane, and $f$, the ratio of biaxial compressive strength to uniaxial compressive strength of concrete, are adopted from Jankowiak et al. [165] While these parameters are provided for concrete, they are used in this study for mortars also, for lack of experimental data on these parameters. The material parameters for XFEM simulation are shown in Table 14. [169,170]

| Table 14: Properties of the mortar and parameters for XFEM simulation |
|-----------------------------|-------------------|-------------------|-------------------|-------------------|
| E(GPa) | $\nu$ | Max. principal stress (MPa) | $G_F$ (N/mm) | CDP model parameters |
| 31.4 | 0.22 | 3.0 | 0.035 | $38^\circ$ | 1.0 | 0.67 | 1.12 |

The uniaxial tension and compression behavior of cement mortar for CDP model are shown in Figure 51. Figure 52 shows the generated load-crack mouth opening displacement (CMOD) response obtained from the XFEM simulation.

![Figure 51: Representative (a) uniaxial tension, and (b) uniaxial compression behavior implemented in the concrete damage plasticity (CDP) model.](image)
Figure 52: Simulated load-CMOD response of the mortar beam using XFEM.

The maximum principal stress contours at three different stages in the load-CMOD response obtained through the implementation of the CDP model in the XFEM framework are shown in Figure 53. Point P-1 in Figure 53 corresponds to 85% of the peak load in the pre-peak regime whereas point P-2 corresponds to 95% of the peak load in the post-peak regime. Point P-3 is chosen at a CMOD value of 0.16 mm, which corresponds to a CMOD very close to ultimate failure. Figure 53a does not show the formation of a crack since the maximum principal stress (2.62 MPa) is smaller than the considered tensile strength (3 MPa) of cement mortar. The crack is observed to initiate close to the peak load when the maximum principal stress equals the tensile strength. Figure 53b shows the stress contour corresponding to 95% of the peak load in the post peak regime. The crack has begun to propagate at this stage and is roughly at the mid-height of the specimen at this load level. The stress concentration near the tip of the crack is also visible as expected. Figure 53c shows almost complete propagation of the crack near failure.

Crack extension-related values at 95% of the peak load in the post-peak regime can be used to calculate the Mode I stress intensity fracture (fracture toughness), $K_{IC}$, of the cement mortar using the two-parameter fracture model (TPFM) as follows: [171,172]

$$ K_{IC} = \frac{PL}{bd^{3/2}} F\left[\frac{a_{eff}}{d}\right] $$  \hspace{1cm} (48a)

$$ F\left[\frac{a_{eff}}{d}\right] = [2.9\left(\frac{a_{eff}}{d}\right)^{1/2} - 4.6\left(\frac{a_{eff}}{d}\right)^{3/2} + 21.8\left(\frac{a_{eff}}{d}\right)^{5/2} - 37.6\left(\frac{a_{eff}}{d}\right)^{7/2} + 38.7\left(\frac{a_{eff}}{d}\right)^{9/2}] $$  \hspace{1cm} (48b)

where the effective crack length, $a_{eff} = a_0 + \Delta a$. The critical crack tip opening displacement (CTOD$_C$), which is another fracture parameter in the TPFM is computed as the CTOD value at 95% of the peak load in the post-peak regime (P-2 in Figure 52). The values of $K_{IC}$ and CTOD$_C$ are 27.4 MPa·mm$^{0.5}$ and 0.012 mm respectively. There is an agreement between the $K_{IC}$ and CTOD$_C$ values obtained from the XFEM simulation and the experimental measurements [173] (26.4 MPa·mm$^{0.5}$ and 0.0125 mm from experimental load-CMOD data, by employing TPFM).
Figure 53: Maximum principal stress contours: (a) P-1 (85% of the peak load in pre-peak regime); (b) P-2 (95% of the peak load in post-peak regime) and (c) P-3 (near failure: CMOD of 0.16 mm).

Figure 54: Images processed using digital image correlation (DIC), with the crack corresponding to the three locations P-1 to P-3 in the load-CMOD plot: (top left) 85% of the peak load in pre-peak regime, (top right) 95% of the peak load in post-peak regime, and (bottom) near failure: CMOD of 0.16 mm.

Digital image correlation (DIC), which is a non-contact optical method that can be used to analyze digital images to extract the full displacement field on a specimen’s surface, [174,175] was used along with the experimental determination of fracture parameters. The time series information from the data acquisition system connected to the loading frame was matched with that from the photographs of the analysis region (images were taken by a CCD camera every 5 seconds) and image correlation was carried out. Figure 54 shows the 2D horizontal displacement fields for the mortar beam corresponding to points P-1 to P-3 in Figure 52. The jump in the horizontal displacement above the notch indicates crack initiation and propagation. [167]
displacement jumps and the visible crack in the images are well correlated, indicated by the dark lines in the images shown in Figures 54. CTOD and crack extension can also be directly measured using DIC, [167] from which the determined \( K_{IC} \) and CTODc values were 30.1 MPa\( \cdot \)mm\(^{0.5}\) and 0.017 mm respectively, which agree well with those determined using the TPFM method and XFEM simulations. Moreover, a comparison of Figures 53 and 54 shows that the crack paths as a function of load are also captured adequately by the XFEM simulations.

3. **Part II: A Continuum-based damage model implemented in MOOSE – simulating volume change induced damage in a hydrating cementitious system**

3.1 **Simulation approach**

XFEM was proposed to be used to detect damage in cementitious materials undergoing radiation-induced deleterious expansions. One of the disadvantages of using XFEM was the need to obtain the concrete damage plasticity (CDP) models for inputs into the model to be used in a finite element analysis package such as ABAQUS. Moreover, the MOOSE framework did not have XFEM incorporated at the time of this work. After discussions with INL, it was decided to use a continuum-based model that can be implemented in MOOSE to determine damage in cementitious materials. Volumetric changes are simulated in the continuum scale using thermal strains imposed on the selected geometry. Considering the large amount of data available for shrinkage in cementitious systems, the restrained ring test was used for simulation. We have developed the MOOSE model and validated it for shrinkage in a restrained ring test. Coupled with the aggregate expansion studies carried out in Task 4, as well as experiments on aggregate expansion, this framework is being implemented for identifying and quantifying damage due to expansive reactions.

Since this is the first implementation of a damage process of a cementitious material in MOOSE, a large part of the study was devoted to identifying and analyzing the fundamental processes of significance in volumetric change induced cracking in cementitious systems. The study has included plain cementitious pastes subjected to volume changes, as well as those containing stiff and compliant inclusions, to ensure that the modeling scheme is robust and can account for different types of concretes.

3.1.1 **Material models**

A flowchart describing the various processes along with the theory to simulate the ring test is shown in Figure 55. The ring test experiments are usually carried out in conjunction with elastic modulus, unrestrained shrinkage and splitting tensile strength tests. The material models which characterize the behavior of early age cementitious materials along with the methodology to determine the material parameters are explained in the following sections.
The viscoelastic nature of cementitious material is modeled using a rate type creep law based on Maxwell chains. [176] While the fracture of the matrix is simulated using the smeared crack approach. [177] While the elastic modulus test describes the aging of elastic modulus of cementitious materials, it is not sufficient to describe the viscoelastic behavior, which occurs during the early age hydration and stiffening of cementitious materials. In the absence of stress relaxation tests, the viscoelastic properties are extracted using the modified correspondence principle [178] (section 3.1.2.1). The stress relaxation curves are then used to obtain the Maxwell chain parameters based on the rate type creep law method (section 3.1.1.1).

The smeared cracking model (section 3.1.1.2) is used to model the fracture in the ring test, while Rankine’s criterion (maximum principal stress exceeding the tensile strength) is used to simulate the fracture initiation. Each finite element was assigned a specific tensile strength based on phenomenological model proposed by Strack et al. [179] (section 3.1.1.3).

3.1.1.1 Rate Type Creep Law

The constitutive relations to describe the time dependent deformation of the early age cement paste can be approximated using generalized Maxwell Model [176] and the generalized Kelvin-Voigt Model. [180] Both these models are equivalent and can be used to describe the viscous behavior of the hydrating cement paste, however, the Kelvin-Voigt model can yield negative spring modulus which is thermodynamically inadmissible. [176] The constitutive relation between stress and strain for a linear viscoelastic material is given by:

\[
\sigma(t) = \int_0^t E_R(t, t') [d\varepsilon(t') - d\varepsilon^0(t')] \tag{49}
\]

where the relaxation modulus, \(E_R(t, t')\) is the stress in the material at time \(t\) due to a unit constant strain acting since time \(t'\). By expanding the relaxation modulus, \(E_R(t, t')\) into Dirichlet series and approximating using the generalized Maxwell model (Figure 56), it could be expressed as:

\[
E^R(t, t') = \sum_{\mu=1}^m E_\mu(t') e^{-\frac{t-t'}{\tau_\mu}} + E_\infty(t') \tag{50}
\]

where, \(m\) is the total number of Maxwell chain. \(E_\mu(t')\) and \(E_\infty(t')\) are the modulus associated with springs in the Maxwell chain and the standalone spring. \(\tau_\mu\) is the relaxation time being implicitly assumed as:
\[ \tau_\mu = \frac{\eta_\mu}{\varepsilon_\mu} \]  

(51)

where, \( \eta_\mu \) is the viscosity of each dashpot.

**Figure 56: Generalized Maxwell model**

3.1.1.2 Smeared Cracking

The smeared crack approach [181] does not track individual macro cracks; instead the effect of cracking is considered through the degradation of material stiffness, and ignores any permanent strain developed due to cracking. The smeared cracking approach requires neither any mesh refinement nor a predetermined crack orientation. The smeared crack approach is also more suitable for distributed fracture. [177] The crack initiates as soon as Rankine’s criterion is met. Once the failure criterion is met, the post failure stress is assumed to decay instantaneously with the strain as shown in Figure 57. The instantaneous decay characterizes the behavior of brittle cementitious material. The fracture energy, \( G_f \) of the specimen undergoing softening with such a mechanism on a finite element of size \( b \) is given by:

\[ G_f = b \int \sigma \partial \varepsilon \]  

(52)

where, \( \int \sigma \partial \varepsilon \) is the area under the stress strain curve. The presence of a mesh size parameter makes the smeared cracking approach mesh sensitive.

**Figure 57: Typical stress-strain curve for the material with post-failure abrupt (instantaneous) strain softening.**

3.1.1.3 Aleatory Uncertainty and Size effect
Stress concentration occurs in heterogeneous materials causing microcracks, which coalesce to form a macroscale fracture, causing some regions in the material to be weaker or stronger than the surrounding material. For cementitious materials, where many cracks coalesce, it becomes quite challenging to predict the failure stress using the deterministic strength-based approach, where a homogeneous strength is assumed at every point in the material. Thus, it is suggested to introduce numerical perturbations in the strength distribution. [179] Without these perturbations, many elements of the axisymmetric ring specimen will reach the failure strength simultaneously causing undesirable response and convergence issues in the FE modeling. A realistic numerical perturbation will give rise to localized strains and stresses and is particularly useful for problems involving bifurcation in a localized state. [182] It was postulated that strength can be characterized as Weibull distributed; however, it is not sufficient to fully describe the cracking. Apart from the numerical perturbations, the strength of brittle materials is highly dependent on the size of the structure. It was suggested that the probability of occurring a critical crack will be higher in a large structure than in a smaller structure. [183] Combining size effect with the Weibull distribution of strength improves the numerical convergence and makes the existing smeared cracking code more robust. Strack et al. [179] proposed a phenomenological model which is given as,

\[ \sigma = \hat{\sigma} \left[ \frac{\hat{V} \ln R}{\hat{V} \ln (1/2)} \right]^{1/m} \]  

where, \( \sigma \) is the strength assigned to the finite element of Volume V and \( \hat{\sigma} \) is the mean strength of sample with volume \( \hat{V} \). R is a uniformly distributed random number which lies in the range \((0,1)\), and \( m \) is the Weibull modulus.

### 3.1.2 Input Parameters

The input parameters for the material models are the Young’s modulus, \( E(t) \), the tensile strength \( \sigma_{tu} \), the relaxation modulus, \( E_r(t,t') \), and the post peak stress strain curve or the fracture parameters. As previously stated, the elastic modulus and the tensile strength are determined from the elastic modulus and splitting tensile strength test. The steps to obtain the viscoelastic parameters are explained in the following section.

#### 3.1.2.1 Determination of viscoelastic parameters

The identification of viscoelastic parameters from the relaxation modulus is straightforward if the relaxation modulus \( E_R(t, t') \) for different \( t' \) values are available using stress relaxation tests or creep tests, by least squares fitting of Equation 49. However, \( E_{\mu}(t') \) are unstable functions of \( E_R(t, t') \) unless \( \tau_{\mu} \) values are selected beforehand and certain smoothing conditions are implemented. [176] Bazant and Wu [176] assumed \( \tau_{\mu} \) as being equal to:

\[ \tau_{\mu} = a^{\mu-1} \tau_1 \]  

where, \( \tau_1 \) can be taken as the time during which the relaxation spectra begin to descend in the log time scale, and \( a \) is the spacing of the relaxation times in the time scale. Thus, \( E_{\mu}(t') \) is obtained through least square regression of the following equation, [176]

\[ \phi = \sum_{\beta} \left( E_R(t_\beta, t') - \hat{E}_R(t_\beta, t') \right)^2 + w_1 \sum_{\mu=1}^{m-1} (E_{\mu+1} - E_\mu)^2 + w_2 \sum_{\mu=2}^{m-2} (E_{\mu+2} - 2E_{\mu+1} + E_{\mu})^2 \]  

where, \( \hat{E}_R(t, t') \) denotes the actual values for the relaxation function, \( \beta \) stands for a series of \((t - t') \) values, \( w_1 \) and \( w_2 \) denote the weights associated with the sum of the squares of the first and second difference of \( E_{\mu} \) as functions of \( \mu \).
As relaxation tests on early age cement pastes are rarely conducted, we extracted the relaxation modulus from the modified correspondence principle [178] by expressing the viscoelastic constitutive equation as per the solidification theory [184] which is given as,

$$
\dot{\varepsilon} = \frac{E_0 \theta(t)}{v(t)} + \frac{1}{v(t)} \int_0^t J^\theta(t - t') \dot{\varepsilon}(t') dt' + \dot{\varepsilon}(t)
$$

(56)

where, $J^\theta(t - t')$ denotes the uniaxial compliance of the aging solid, $E_0$ is the elastic modulus at age where the aging function, $v(t)$ equals unity. The aging function is expressed as,

$$
v(t) = \kappa \left(1 - \exp(-\lambda(t + t'))\right)
$$

(57)

where, $\kappa$ and $\lambda$ are fitting parameters which can be obtained by elastic modulus normalized at age $t'$ when the loading starts. Using this aging function, Grasley and Ambrosia [178] modified the existing correspondence principle and expressed the constitutive relation of solidification theory in Laplace domain as,

$$
\sigma(s) = \kappa E_R(s) \left\{ (se\varepsilon(s) - (s + \lambda)e(s + \lambda)/e^{\lambda t'}) - (se'\varepsilon(s) - (s + \lambda)e'(s + \lambda)/e^{\lambda t'}) \right\}
$$

(58)

where, $\sigma(s)$, $\varepsilon(s)$, $e'(s)$ are the stresses strain and free strain in the Laplace domain. $E_R(s)$ is the non-aging viscoelastic Young’s modulus. Inversion of $E_R(s)$ into time domain yields $E_R(t - t')$, the non-aging viscoelastic Young’s modulus in time domain. Multiplying this with the aging function gives the aging viscoelastic modulus.

3.1.2.2 Determination of Fracture Parameters

The failure is assumed to occur as soon as Rankine’s criterion is met, i.e., stress is greater than the strength of the material. Due to the low strength and brittle nature of cementitious mixtures, it cracks immediately, indicating that it is characterized by a low fracture energy. It is difficult to obtain the early age fracture properties of cement paste; as a result, there is paucity of detailed information of fracture properties of early age cement paste. The fracture energy of cement pastes and mortar has generally been ascribed as 20-25 N/m and 25-30 N/m at 28 days in the literature. [168,185,186] The fracture energy obtained from the simulations will be compared against these values. The mean strength in Strack’s formula was taken as the actual failure stress if there was significant difference in the failure stress and the splitting tensile strength. The Weibull modulus was taken as 24, which is what is generally prescribed for cementitious materials. [183]

3.1.3 Temperature to simulate volume change

The unrestrained drying test is usually accompanied with the ring test. It is this drying of cementitious materials which, if restrained, causes cracking. It is difficult to simulate the effect of drying shrinkage on the cementitious ring directly. The ring test is, thus, simulated with a fictitious temperature drop, which is designed to relate free shrinkage of the cementitious paste in the restrained ring. The fictitious temperature is calculated by dividing the unrestrained (free) shrinkage of the specimen by the coefficient of thermal expansion of the mix as:

$$
\Delta T_{eq} = \frac{\varepsilon_{FS}}{\alpha}
$$

(59)

where, $\Delta T_{eq}$ is the equivalent change in temperature applied to the cementitious mixture, $\varepsilon_{FS}$ is the free shrinkage, and $\alpha$ is the linear coefficient of thermal expansion. The fictitious temperature is applied only to the cementitious mix. However, for this method to be successful the drying conditions (relative humidity, temperature) in both the ring specimen and unrestrained shrinkage specimen should be identical. Also, uniform drying from the top and/or bottom surface should be ensured. In case of a differential drying from the surface, differential temperature should be applied in the numerical simulation.
4. **Finite Element Implementation**

The finite element implementation of ring test is carried out in MOOSE, [187] which is an open source object oriented finite element framework. The object-oriented nature of MOOSE enables the addition of modules to treat viscoelasticity and aleatory uncertainty to better suit the ring test simulations.

4.1 **Finite Element Model**

A two-dimensional plane stress FE model is used to characterize and compute the mechanical response of the cementitious mixtures. Using symmetry boundary conditions, one-quarter of the model is used as shown in Figure 58b. The outer ring has not been modeled, as the paste shrinks and loses contact with the outer ring and the shrinkage is only restrained by the inner ring. Although the cement paste initially expands and then starts to shrink, the initial expansion is ignored by the FE model. The initial expansion, which is usually caused by the heat generated by early age cement hydration, [188] is ignored as the objective of the current work is to assess cracking of the cementitious paste undergoing drying shrinkage. The ring and cement paste are modeled as separate parts with a frictionless contact acting between the two parts to mimic the actual experiment, where a form release agent is usually applied on the rings to minimize bonding with cementitious mixture.

![Figure 58: (a) Schematic view of the dual ring and the (b) finite element model used in this study. The dimensions are provided in the table.](image)

<table>
<thead>
<tr>
<th>Radius</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
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<tbody>
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<td>mm</td>
<td>mm</td>
<td>mm</td>
</tr>
<tr>
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<td>50.8</td>
<td>76.2</td>
<td>82.6</td>
</tr>
<tr>
<td>Validation Test</td>
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<td>150</td>
<td>225</td>
<td>-</td>
</tr>
</tbody>
</table>

5. **Verification tests**

5.1 **Ring test with and without inclusions**
A dual ring geometry containing cementitious pastes has been previously used [188] to assess the cracking tendency of cement paste and paste with phase change material (PCM; a compliant inclusion) or quartz inclusions. The same geometry with cementitious mixtures enclosed in dual Invar rings is used as shown in Figure 58. The plain cement pastes and pastes with inclusions were kept in a programmable environmental chamber under partially sealed conditions for the first 7 days at 25°C and 87% relative humidity (RH). The top surface was covered with PVC sheets whereas the ring was kept on an acrylic base. The gap between PVC sheets and the concrete ring allowed uniform moisture loss from the ring specimen. After 7 days, the top PVC sheet and bottom base were removed, and the rings were kept on elevated wire mesh platform. The rings were also exposed to more aggressive drying at 50% or 75% RH to accelerate the cracking time. There are four strain gauges installed at the middle height of each inner and outer ring. A sudden drop in the strain readings indicates the initiation of crack. It was observed that PCM inclusions substantially improved the cracking tendency of the cementitious composites by delaying the cracking time, even though they do not affect the tensile capacity of the cementitious composites. The delay in cracking time was attributed to the slower rate of damage accumulation in the PCM containing cementitious composites. The specimens dried at 50% RH also experienced accelerated cracking compared to specimens dried at 75% RH due to faster damage accumulation in the former and a shorter time available for stress relaxation.

5.1.1 Loading and Boundary Condition

The fictitious temperature applied to the ring specimen for different cases is shown in Figure 59. It was noted that the addition of “stiff” or “soft” inclusions does not alter the unrestrained shrinkage. [189] Expectedly, the applied fictitious temperature does not change much for plain paste and quartz inclusions due to the similar coefficients of thermal expansion. The addition of PCM, however, increases the coefficient of thermal expansion which results in a decrease in the applied fictitious temperature. The boundary conditions are shown in Figure 58b.

![Figure 59: Applied Temperature Change as a function of age to simulate shrinkage](image)

5.1.2 Material Properties

Invar rings are defined by linear elastic properties. The elastic modulus, Poisson’s ratio and coefficient of thermal expansion for Invar ring have been taken as 141 GPa, 0.28 and 2.5 με/°C. The time dependent elastic modulus and cracking stress was obtained from Wei et al. [190] for different mixes respectively. The stress relaxation curves (viscoelastic modulus) for different cementitious mixtures, shown in Figure 60, were obtained in two parts. For the first 7 days, the viscoelastic modulus was obtained using the modified correspondence principle using the ring
strain data. After 7 days, the cementitious mixture is subjected to aggressive drying, resulting in cracking soon afterwards. It was difficult to extract the viscoelastic parameters from the correspondence principle for such a small interval due to limited stress and strain data. Thus, the viscoelastic parameters were obtained by matching the residual stress development in the ring with the numerical simulations by assuming Maxwell Coefficients. From Figure 60, it can be observed that the modulus at age $t'=1$ day drops from $\sim5000$ MPa at time $= 1$ day to $\sim180$ MPa at time $=5$ days for plain paste and paste with quartz inclusions. The high stress is due to the higher elastic modulus gain in such materials. For paste with 10% PCM inclusions, the modulus decreases from $\sim3300$ MPa at time $= 1$ day to $\sim 161$ MPa at time $= 5$ days. For paste with 20% inclusion, the modulus at $t'=1$ drops from $\sim 2500$ MPa at time $= 1$ day to $\sim 64$ MPa at time $= 5$ days. Therefore, the pastes with low dosages of inclusions exhibit similar viscoelastic parameters as the plain paste. Pastes with higher dosages of compliant inclusions exhibit less relaxation than the plain paste but the resultant stress is also lower. This agrees with the results obtained by Wei et al. [189] Beyond 7 days, the relaxation reduces for all the pastes as the drying rate increases.

![Graphs showing viscoelastic modulus of cement pastes](image)

**Figure 60:** Viscoelastic modulus of cement pastes. The black lines correspond to the viscoelastic modulus at different age $t'=1, 2, ..., 7, 7.5$ days.
The Maxwell chain parameters (relaxation spectrum), calculated for the cementitious mixtures from the stress relaxation curves (before 7 days), are shown in Figure 61. As expected, the values are similar for the neat paste and the paste with 10% quartz inclusions, asserting the fact that the addition of quartz inclusion does not affect the elastic/viscoelastic parameters as much as compliant inclusions do. It can be observed, that $E_\infty$ suddenly increases on aggressive drying indicating that the process is becoming increasingly elastic. This is expected as aggressive drying hardens the material quickly and thus the elastic contribution increases rapidly.

![Graphs showing relaxation spectrum for different cement pastes](image)

**Figure 61:** Maxwell Chain parameters of cement paste. (a) Plain OPC, (b) Paste with 10% PCM inclusions, (c) Paste with 20% PCM inclusions, and (d) Paste with 10% quartz inclusions.

5.1.3 **Comparison of experimental results with the simulation**

Figure 62 shows the experimental residual stress development for all the four cementitious mixtures along with the simulation results. The residual stress from the simulations correspond to the average hoop stress in all the inner elements. The experimental data correspond to the residual stress calculated from the strain measurements of the four strain gauges. Despite the limited data available, the predicted cracking time using the ring test data match well the experimental values. The simulation results are consistent with the observation that the addition of compliant PCM inclusions increases the cracking time. The increase in cracking time is attributed to improved stress relaxation with the addition of compliant inclusions. The same increase in relaxation is not observed when more stiff inclusions such as quartz are added. The addition of PCM inclusions also reduces the stress in the cementitious mixtures. This is because of greater stress relaxation and reduced elastic modulus that manifest with the addition of more compliant inclusions. Expectedly, the addition of inclusions at higher dosages further reduces the stress (notice the stress...
at 7\textsuperscript{th} day from Figure 62b and 62c). The cracking time is enhanced when the mixtures are dried at 75\% RH than at 50\% RH. When the mixtures are dried at a lower ambient RH, it causes rapid moisture loss causing the steep rise in the drying shrinkage.
Figure 62: Residual stress development in the cementitious mixtures as a function of drying time and RH. (a) Plain Cement Paste, (b) Paste with 10% PCM inclusions, (c) Paste with 20% PCM inclusions and (d) Paste with 10% Quartz inclusions.

6. Validation tests
6.1 Ring test with different restraining ring thickness and different initial moisture conditions

Ring test simulations were carried out on cement-sand mortar specimens with different restraining steel ring thickness (3.1 mm, 9.5 mm, and 19 mm) for two water-to-cement ratios (w/c; 0.3 and 0.5). [190] The specimens with lower w/c contained water reducing admixtures. The analysis concluded that a higher restraint causes greater stress relaxation and earlier age of cracking. The high initial w/c also causes a delay in cracking owing to lower stress, which is a result of lower elastic modulus development in the specimen with higher w/c. The dimension of ring setup is shown in Figure 58. The three dimensions of ‘a’ correspond to the three sizes of the inner ring.

6.1.1 Loading and Boundary condition

The applied fictitious temperature as per the free shrinkage of the specimen, as explained in Section 5.1.1, is shown in Figure 63.

Figure 63: Applied temperature change as a function of age to simulate shrinkage.

6.1.2 Material Properties
The elastic modulus, Poisson’s ratio and coefficient of thermal expansion for the steel ring are taken as 200 GPa, 0.3 and 7.2 με/°C. The time dependent elastic modulus and failure stress are also available in the literature for these mixtures. [190] The viscoelastic modulus of the mortars are shown in Figure 64. From Figure 64, it can be seen that, as the size of restraining ring increases, the stress relaxation increases. This is in line with the reported observations. [190] However, the effect is more pronounced in paste with a w/c of 0.3.

![Figure 64: Viscoelastic modulus of cement sand mortar for (a) 0.3 and (b) 0.5 water to cement ratio. The straight, dashed, dashed-dot line correspond to the viscoelastic modulus for ring thicknesses of 3.1mm, 9.5 mm, and 19.1 mm at different age $t'=1,5,10, \ldots25$ days for w/c ratios of 0.3 and 0.5.](image)

### 6.1.3 Comparison of experimental results with simulation

Figures 65 shows the residual stress development from the numerical simulations, shown along with the experimental values. The specimen with a ring thickness of 19 mm cracked prior to reaching its tensile strength and thus these results are not shown here. The ring with higher restraint exhibited a greater build-up of stresses even though relaxation is greater; thus, cracking occurs earlier in agreement with FE simulations.
6.2 Validation on a 3D ring simulation to consider moisture gradient

Our objective is to test how well the framework can predict damage in a 3D simulation, considering the moisture gradient in the ring as it dries from the top and bottom surface. The simulation approach is broadly similar to that described in the previous section. Ring test simulations were carried out on cement-sand mortar specimens \( \text{w/c} = 0.5 \) with restraining steel ring thickness of 9.5 mm and cement mortar ring thickness of 75 mm. The depth of cementitious ring is 75 mm (Figure 65b).

6.2.1 FE Model, Boundary condition and Loading

Figure 66 shows the 3D FE model and the associated boundary conditions. Due to symmetry, one eight of the full 3D model is used. In the 2D simulation, the free shrinkage was applied as the temperature loading over the entire surface (see Figure 63). In this work, shrinkage will be considered as varying with the pore humidity over the depth of the specimen. The pore humidity inside the depth ‘\( x \)’ from the surface at time ‘\( t \)’ is estimated as: [160]

\[
H(x, t) = H_1 - (H_1 - H_5)erfc(x / \gamma)
\]

where, \( H_1, H_5 \) are the pore humidity at the center of a sealed specimen at the end of 1 day and at the surface of the exposed specimen (taken as 0.97 and 0.5 respectively). \( H_1 \) has been taken as 0.97 to account for autogenous effect. \( \gamma \) considers the moisture diffusion (characterized by coefficient \( D \)) and is equal to:

\[
\gamma = 2\sqrt{D}t
\]

\( \gamma \) is found to vary linearly with time as:

\[
\gamma = 0.18t + 6
\]

where ‘\( t \)’ is the time in days. The drying shrinkage \( \varepsilon_{SH} \) is then assumed to vary linearly with humidity as per the following equation

\[
\Delta\varepsilon_{SH}(t) = \varepsilon_{SH-\infty}g_s(t)\Delta H
\]

where, \( \varepsilon_{SH-\infty} \) is the ultimate shrinkage taken as 718.225 με, [190] \( \Delta H \) represents the change in humidity and \( g_s(t) \) is the ratio of the ultimate elastic modulus to the current modulus at time ‘\( t \)’. To avoid the sudden change in the humidity at the boundary, Bazant consider an additional surface thickness of 0.75 mm. [192] The distribution of humidity and shrinkage inside the specimen using...
the above formulation is shown in Figure 67. The varying shrinkage over depth is applied as a varying temperature loading over the depth as specified in section 3.1.3.

![Figure 66: 3D FE model used in the study with the associated boundary condition.](image)

### 6.2.2 Material Properties

The elastic modulus, Poisson’s ratio, and coefficient of thermal expansion for the steel ring are taken as 200 GPa, 0.3 and 7.2 με/°C. The viscoelastic modulus of the mortar is shown in Figure 64b. The cracking condition was switched off for these simulations as it was observed that the rise in stress is too high in the simulations as shown in section 6.2.3.

![Figure 67: (a) Humidity and (b) shrinkage profile inside the specimen.](image)

### 6.2.3 Comparison of experimental results with simulation

Figure 68 shows the result of FE simulations and comparison with the experiments. The moisture gradient gives a sudden increase in shrinkage at the top of the specimen (see Figure 68b). In the FE simulations this causes a sudden rise in the stresses at the top layer which cracks quite early (the maximum stress in the top layer is reached in 5 days as opposed to 20 days in the experiment). The experimental stress has been calculated based on the strain measurements of the ring test by assuming uniform shrinkage over the depth of the specimen. The 2D plane stress assumptions, therefore, match the experimental results (see Figure 65b). For the 3D simulations to correctly estimate the cracking time, accurate predictions of the shrinkage and creep characteristics are required. A shrinkage model which considers the nonlinear dependence on humidity [192] and a humidity-based creep model [193] will be used in the future simulations.
7. Summary
A finite element framework has been developed in MOOSE to assess the cracking potential of cementitious mixtures under early age volume changes. The framework considers the viscoelastic behavior of early age cementitious materials using the rate type creep law. The viscoelastic properties were obtained using the modified correspondence principle. The framework also considers the spatial variation in strength using a phenomenological model to consider the effect of microcracks and ensure better convergence. The framework has been tested against experimental studies reported in the literature. The proposed framework predicts an increase in cracking time, and a reduction in stresses with the addition of compliant inclusions into a cementitious matrix. The framework also correctly predicted higher stresses and earlier cracking time for rings with thicker restraints for two different water to cement ratios. The implementation of this framework in MOOSE enables the validation of the cracking phenomenon due to volume changes. Shrinkage cracking was considered in model development since there is a large amount of data available in the literature, whereas not enough expansive aggregate-related data is available.

Summary and Conclusions

This study has clarified the extent to which neutron irradiation induces atomic scale alterations for a variety of minerals of a wide range of chemical composition and crystallographic structure, and applied these findings in the development of a mechanistic degradation model for concrete undergoing irradiation-induced expansion. The effects of neutron irradiation were simulated using Ar⁺ ion irradiation, and the reactivity of the solids were taken as their aqueous dissolution rate measured using vertical scanning interferometry in solutions of different alkalinites. The silicates quartz, almandine, and albite, and the carbonates calcite and dolomite, upon irradiation, exhibited varying degrees of structural alteration. The experimentally determined enhancements in dissolution were rationalized using density and topological constraints analyses carried out using molecular dynamics simulations, showing that network rigidity changed in the silicates and carbonates, to different extents. In silicates, the dissolution enhancement can be related to the degree of polymerization of the initial solids and the dissolution mechanisms that persist. The carbonates, which feature an ionic structure showed minimal structural changes and corresponding
dissolution rate enhancement, owing to the prevalence of ionic bonds which recover upon removal of the irradiation stimulus.

The thermodynamic properties of Na- and K-based alkali-silica reaction (ASR) gels were established, revealing that the solubility of ASR gels is influenced by both its composition and the aqueous temperature. For instance, the presence of Al in the solid in a reduced solubility of the ASR gel. From the GEMS-based models of gel phase assemblages, the susceptibility toward formation of expansive ASR gels for a given solution composition was derived. Further, an extended finite element framework was developed to characterize the damage in cementitious materials undergoing degradation caused by aggregate expansion. Thermal strains were applied to simulate microstructural expansion, and the extent of expansion was evaluated for three different aggregates introduced as inclusions. The microstructure-based XFEM was implemented in a mesoscale continuum structure to evaluate crack propagation. The continuum damage framework was then implemented in the MOOSE environment to evaluate the thermal, creep, and neutron fluence-induced damage in aggregates and mortar. The coupled expansion and damage model thus developed was validated against experimental results. The proposed framework predicts an increase in time for cracking and a reduction in stresses with the incorporation of compliant inclusions into a cementitious matrix, and earlier cracking for rings having thicker restraints. The implementation of this framework in MOOSE enables the validation of the cracking phenomenon resulting from volume changes by shrinkage.

Thus, by the integration of atomic, microscale, and mesoscale investigations, an understanding of irradiation-assisted aggregate-induced degradation in nuclear power plant concretes was obtained. Evolutions in mineral dissolution, ASR gel precipitation, and aggregate expansion-induced cracking were considered to evaluate the tendency for and the effects on concrete durability of enhanced alkali-silica reactions in the presence of irradiation. These findings can be applied to determine characteristics of durable concrete and estimate damage in existing concretes in consideration of second license renewals of nuclear power plants.
References


