Effects of neutron irradiation on densities and elastic properties of aggregate-forming minerals in concrete

Weiping Zhang a, b, Hui Liu a, b, Yong Zhou a, b, *, Kaixing Liao b, c, **, Ying Huang c

A R T I C L E   I N F O

Article history:
Received 10 September 2022
Received in revised form 9 March 2023
Accepted 17 March 2023
Available online 20 March 2023

Keywords:
Concrete
Aggregate-forming minerals
Swelling
Molecular dynamics
Radiation damage

A B S T R A C T

The aggregate-forming minerals in concrete undergo volume swelling and microstructure change under neutron irradiation, leading to degradation of physical and mechanical properties of the aggregates and concrete. A comprehensive investigation of volume change and elastic property variation of major aggregate-forming minerals is still lacking, so molecular dynamics simulations have been employed in this paper to improve the understanding of the degradation mechanisms. The results demonstrated that the densities of the selected aggregate-forming minerals of similar atomic structure and chemical composition vary in a similar trend with deposited energy due to the similar amorphization mechanism. The elastic tensors of all silicate minerals are almost isotropic after saturated irradiation, while those of irradiated carbonate minerals remain anisotropic. Moreover, the elastic modulus ratio versus density ratio of irradiated minerals is roughly following the density–modulus scaling relationship. These findings could further provide basis for predicting the volume and elastic properties of irradiated concrete aggregates in nuclear facilities.

© 2023 Korean Nuclear Society, Published by Elsevier Korea LLC. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Concrete applies widely in the construction of nuclear facilities owing to its excellent radiation shielding and structural load-bearing capabilities, such as in biological shielding walls around reactor pressure vessels [1–3] and solidification of spent nuclear waste [4]. Irradiation experiments have shown that the radiation-induced volumetric expansion (RIVE) of concrete aggregates, which are composite of various minerals and take roughly 70% of the concrete volume, is the primary damage mechanism of irradiated concrete [5,6]. At the atomic scale, the amorphization of aggregate-forming minerals upon irradiation is the most important mechanism for their volume change and mechanical property degradation [7–9]. The volume expansion of different minerals in aggregates causes microcracks or macroscopic fractures within the aggregates and concrete, which results in the degradation of the macroscopic physical and mechanical properties of concrete [10–12]. Therefore, investigating the effects of neutron irradiation on the volume and mechanical properties of the major aggregate-forming minerals is essential for predicting and improving the lifetime of concrete structures.

Aggregates in concrete for nuclear power plants are generally composed of abundant silicate minerals or carbonate minerals, such as quartz, feldspars, micas, clay minerals, calcite, and dolomite [6,7]. The irradiation experimental data of minerals mainly focus on the study of the size changes of quartz under neutron fluence [7,13–17], and there are fewer studies on the volume change of feldspars, micas, and clay minerals [8]. Meanwhile, the effect of irradiation on the degradation of mechanical properties of these major aggregate-forming minerals has not been fully understood. Moreover, the available experimental results have several limitations [8,16]: (1) The irradiation experimental data for some minerals at high fluence are relatively scarce, hence the maximum volume changes of the minerals are difficult to determine accurately (2) The volume changes of some silicate minerals (e.g., quartz and feldspars) are strongly dependent on the boundary conditions.
The structural evolution of silicate minerals at different irradiation temperatures needs to be clarified [18]; (3) The presence of microcracks or fractures within natural feldspar samples under irradiation would overestimate their volume expansion. Besides, the differences in the RIVE of feldspars have been known, while the effect of the Na–K–Ca substitution for feldspars is insufficiently studied in the open literature [8], which is important for the identification of volume changes of feldspars and the strengthening of knowledge base; (4) Phyllosilicates are difficult to experiment with due to their almost perfect basal cleavage, causing the data on phyllosilicates to be scarce. Whether the apparent sudden increase of RIVE in muscovite is due to an actual physical mechanism remains to be determined.

The neutron cascade collisions and disordering processes of minerals can be simulated by molecular dynamics (MD) at the atomic scale [14], and this method is used herein to investigate the effects of neutron irradiation on the volume and elastic moduli of the major aggregate-forming minerals in concrete. There are several MD simulations of densities and elastic properties of some silicate minerals under irradiation [14,17,19–22]. In this study, the densities and elastic moduli of eight aggregate-forming minerals were simulated, and these minerals are representative of common minerals in concrete aggregates [6]. Including quartz, albite, anorthite, microcline, sericite, chlorite, calcite, and dolomite. The potential and mechanism of the volume change of these minerals were investigated. For quartz, irradiation simulations at different temperatures were also performed to investigate the temperature effect; for feldspars, three typical feldspars were selected to investigate the effect of Na–Ca–K substitution on the RIVE.

2. Simulation details

2.1. Mineral crystalline model

The eight single-crystal minerals, i.e. quartz [23], albite [24], anorthite [25], microcline [26], sericite [27], chlorite [28], calcite [29] and dolomite [30] were also found to be commonly observed and abundant minerals in concrete aggregates for nuclear power plants in China. The atomic structure parameters of the pristine minerals can be obtained from the respective references. These minerals can be classified as either silicate minerals or carbonates. The specific topologies of silicate minerals are mainly controlled by the degree of polymerization of the [SiO4]4− tetrahedra [31]. Quartz, albite, anorthite, and microcline are tectosilicates, while sericite and chlorite are phyllosilicates. Carbonate minerals such as calcite and dolomite have island structures [29,30] and are composed of metal ion bonded [CO3]2− with an ionic bond. The crystal structures of these minerals are described in detail below.

2.1.1. Quartz and feldspars: quartz, albite, anorthite, and microcline

Quartz is a typical silicate mineral characterized by a three-dimensional 6-member Si ring network [23]. It presents various polymorphs depending on the temperature and pressure conditions of formation. The α-quartz in a trigonal system is fused in this study, which is stable at low temperature and pressure [32].

Albite, anorthite and microcline have 4-member Si ring and 6-member Si ring structures, with heavier cations located at spacious channels in the silicate network. Feldspars (KAlSi3O8−NaAlSi3O8−CaAl2Si2O8) are generally classified into plagioclase (e.g., albite and anorthite) and alkaline feldspars (e.g., microcline), and the sodium ions abundant in albite can be partially or completely substituted by calcium or potassium ions. Albite and anorthite are the end-members of plagioclase for sodium [24] and calcium [25], respectively. Microcline is one of the three polymorphs with orthoclase and sanidine, and orthoclase is the potassium-rich end-member of alkali feldspars [26]. All the three minerals exhibit a triclinic crystal structure composed of Si–O or Al–O tetrahedra, with the respective cations acting as charge-compensating to balance the charge of the tetrahedral units, and all O atoms existing in the crystalline are bridging oxygens, which refers broadly to all polyhedral shared oxygen atoms except hydroxyl oxygen. Albite, anorthite and microcline were selected herein as representative feldspars in concrete aggregates to investigate the effect of Na–K–Ca substitution on feldspars RIVE.

2.1.2. Micas and clay minerals: sericite and chlorite

Phyllosilicates such as micas and clay minerals are significantly less than tectosilicates in concrete aggregates [33]. Predicting the actual maximum RIVE of different phyllosilicates is difficult due to the great differences in their chemical composition. In this study, the irradiation responses of sericite and chlorite were analyzed.

The most common form of micas is muscovite (di-octahedral layered structure), while numerous atoms substitutions are observed in various geological environments. Muscovite is composed of a Si–O tetrahedral 6-membered ring inserted between the K+ and Al–O layers. Sericite is a fine-grained (generally grain size <0.01 mm) variety of muscovite minerals [27]. Clay minerals are layered hydrated aluminosilicates composed of Si–O tetrahedral (T) sheets and Al–O octahedral (O) sheets, and these basic sheets are combined into TO and TOT layers. Clay layers charged negatively resulting from the substitution of Al3+ (or Fe3+) for the tetrahedral Si4+ or Mg2+ (or Li+) for octahedral Al3+, which are balanced with hydrated cations like Na+ and Ca2+ occurring in the interlayer [34]. The chlorite crystal chosen here is plagioclase chlorite (magnesium-rich chlorite), which is commonly known as chlorite [28]. Chlorite is composed of Si–O tetrahedral 6-membered rings inserted between Mg/Al–O layers and interlayer Mg2+/Al3+ cations.

2.1.3. Carbonate minerals: calcite and dolomite

In this study, the irradiation responses of calcite and dolomite were analyzed. Calcite and dolomite have a similar structure in which carbonate ion ([CO3]2−) layers separate the different cation layers (Ca2+ in calcite, or Ca2+ and Mg2+ in dolomite) [29,30]. Both minerals exhibit a trigonal crystal structure, while the alternating Ca–Mg arrangement in dolomite reduces its symmetry.

2.2. Simulation method

The open-source LAMMPS (Massive Atomic/Molecular Massively Parallel Simulator) [35] MD software package was used to simulate the irradiation-induced cumulative damage progress of the selected minerals, following a well-established methodology [14,22,36–40] described below. The atomic structures of all pristine minerals were relaxed in the isothermal-isobaric ensemble (NPT) at 300 K and 0 atm for 20 ps, and the crystalline structure was in equilibrium and had no residual stress before the next irradiation simulation. The average structural and thermodynamic properties of the equilibrium structures were calculated from the MD simulation continued for another 20 ps.

2.2.1. Neutron irradiation simulation

The irradiation simulation at 300 K was carried out as follows. First, the target atom in the mineral supercell was randomly selected as the primary knock-on atom (PKA) based on the weighted probabilities of the respective elements, and then the atom was accelerated with a kinetic energy of 600eV. The selection of kinetic energy was confirmed to not affect the final topology of the atomic structure. The PKA with 600 eV deposited energy...
corresponds to the incident neutron energy approximately ranging from 3-to-14 keV based on the expected energy loss of the colliding neutrons, and the scattering cross sections were calculated by integrating over the energy region of 3-to-14 keV [19,22]. The fraction of total energy deposited to each element was chosen based on its scattering cross section (see Table 1). The accelerated atom then collided with the other atoms in the crystalline resulting in a ballistic cascade in a random direction, while the irradiation-induced velocity of the accelerated atom depends on the atomic mass. The ballistic cascades were treated in the microcanonical (NVE) ensemble to minimize the effects of the thermostat on the dynamic progress after impact. Once the PKA stopped, a spherical region of 10 Å was built around the PKA as the center. It should be noted that “stop” refers to a condition that the total cascade displacement of the PKA was less than 1 Å during 1 ps. The atoms in the spherical region were treated in the microcanonical (NVE) ensemble, while the outside atoms were in the isothermal-isobaric ensemble (NPT) at 300 K by a Berendsen thermostat [41]. These ensembles ensured the temperature gradually returned to 300 K. A variable timestep was employed during the ballistic cascade, and the fixed timesteps of 0.5 fs, 1 fs, and 1 fs were employed during the rest of the simulation for ReaxFF [42], Teter [43], and ClayFF [44] potential, respectively. The dynamical simulation of the cascade collision process was lasting for 15 ps, which is sufficient to ensure the convergence of the temperature and energy calculations. The system was further relaxed in an isothermal-isobaric ensemble (NPT) after each cascade collision at 300 K and 0 atm for another 5 ps. Finally, the process was repeated until both the density and enthalpy of the mineral system had reached a plateau. Note that the final atomic structures of minerals are almost the same after the saturation of defects, though there are multiple mechanisms of amorphization observed in minerals upon irradiation [19,39,45,46]. Therefore, the mineral density with final saturated irradiation provides an assessment of the maximum volume change of the mineral.

To limit the computational expense, the size of the supercell system was determined to be more than twice as large as the maximum distance of the PKA cascade during 1 ps [19]. It ensured that the computational cost was small enough and the spurious self-interactions resulting from the periodic boundary conditions could be avoided during the ballistic cascade. The supercell’s size parameters used and the number of PKAs calculated for each mineral are listed in Table 2.

2.2.2. Interatomic potentials

The reliability of MD simulations relies heavily on the accuracy of the interatomic potentials. The interatomic potential for irradiation simulations must accurately describe not only the pristine and disordered structures with a fixed set of parameters, but also the short-range high-energy and high-velocity interactions resulting from the ballistic cascade. The optimal potentials were selected herein for different minerals based on their abilities of predicting the structure, density, and elastic properties of the pristine mineral and the corresponding glass.

ReaxFF [42] was used for quartz, and this potential allows to predict the atomic structure of both quartz and silica glass [47]. For feldspars, the Buckingham potential parameterized by Teter [43] was used. This potential has been widely used and can predict the atomic structure of various silicate glasses [19,37,48]. This forcefield includes Coulombic interactions, an exponential short-range repulsion term, and a longer-range van der Waals term. Its short-range interactions are in the Buckingham form:

$$U_{ij} = A_{ij}e^{-r_{ij}/\rho_i} - C_{ij}/r_{ij}^6 \quad (1)$$

where $U_{ij}$ is the interatomic potential energy of atom $i$ and $j$; $r_{ij}$ is the interatomic distance; $A_{ij}$, $\rho_i$, and $C_{ij}$ are the parameters fitted for each pair of atoms. The longer-range Coulombic interaction is set with fixed partial ionic charges to consider partial covalency in silicate and aluminate systems. The partial charge for oxygen is $-1.2e$, and the partial charges of the other atoms are scaled proportionally from their formal charges to ensure the charge neutrality of the whole system. The parameters of Teter potential used herein are summarized in Table 3 [43]. The Ziegler-Biersack-Littmark (ZBL) potential was splined with Teter potential to describe the short-range repulsive interactions during the ballistic cascades [49].

For sericite and chlorite, CLAYFF [44] including Coulombic interactions, short-range van der Waals interactions, and bonded (stretching/angular) interactions was used. CLAYFF has been parameterized to simulate layered minerals with permanent charge, and the interaction parameters between different atoms are calculated according to the mixed rules. This forcefield is applicable and widely used to predict the atomic structure and elastic properties of disordered phyllosilicates [34,50–52].

For calcite and dolomite, the potentials of Raiteri et al. [53,54] were used. This forcefield also relies on the Buckingham form and has a different set of parameters shown in Table 4. Note that carbonate groups are modeled as rigid molecules by a harmonic potential [53,54]. This forcefield is used to accurately predict the atomic structure of crystalline and amorphous carbonates [22,53,54].

3. Results

3.1. Density and structural evolution of aggregate-forming minerals upon irradiation

The crystal structure of minerals upon irradiation is significantly affected by altering the coordination numbers, bond lengths, bond angles and their medium-range order, and the properties of the whole crystal are altered because of the defect accumulation in atomic structure. The differences in the atomic structure of pristine and irradiated minerals were analyzed by calculating the PDF (pair distribution function) $g(r)$ [55]. Otherwise, the available experimental data of irradiated minerals was used to verify the results of MD simulations.

3.1.1. Density and structure of the pristine minerals

During the initial relaxation, the crystal structures of the pristine minerals are stable enough with no alterations in box sizes, coordination numbers, bond lengths, and angles. To verify the ability to predict realistic structures for the pristine minerals, the densities of all eight pristine minerals relaxed at 300 K were calculated to compare with their experimental data [24–30] (see in
As shown in Fig. 1, the simulated densities of the pristine minerals are in good accordance with their experimental data.

### 3.1.2. Normalized density evolution of silicate minerals

Fig. 2 shows the normalized density evolutions of all six silicate minerals as a function of the deposited energy. The densities of silicate minerals exhibit significantly different trends, which may increase or decrease [19]. For albite, anorthite, and microcline, their densities increase slightly with the deposited energy. For quartz, sericite, and chlorite, their densities decrease steeply. It is observed that silicate minerals with similar atomic structure and chemical composition have a similar trend in density variation. Otherwise, the equilibrium density of quartz is reached at higher deposited energy relative to the other silicate minerals.

### 3.1.3. Density and structural evolution of quartz and feldspars

As shown in Fig. 3(a), the density evolution of quartz exhibits a significant decrease trend as a function of the deposited energy, and its final equilibrium density is stabilized at 2.18 g/cm³, which is consistent with the density of 2.20 g/cm³ (maximum RIVE of 17.8%) as shown in Fig. 1. The simulated densities of the pristine minerals are in good accordance with their experimental data.

### Table 2

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Number of atoms (Size parameters)</th>
<th>Composition (Number of PKAs)</th>
<th>Density (ρ, g/cm³)</th>
<th>Elastic modulus (E, GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Initial</td>
<td>Final</td>
</tr>
<tr>
<td>Quartz</td>
<td>8100 (10 × 10 × 9)</td>
<td>SiO₂ (335)</td>
<td>2.66 (2.64 [23])</td>
<td>2.18 (2.20 [12])</td>
</tr>
<tr>
<td>Albite</td>
<td>9984 (4 × 6 × 8)</td>
<td>NaAlSi₃O₈ (240)</td>
<td>2.65 (2.62 [24])</td>
<td>2.66 (2.59° [7])</td>
</tr>
<tr>
<td>Anorthite</td>
<td>8320 (5 × 4 × 4)</td>
<td>Ca₂Al₂Si₄O₁₀ (345)</td>
<td>2.72 (2.76 [25])</td>
<td>2.86</td>
</tr>
<tr>
<td>Microcline</td>
<td>9984 (6 × 4 × 8)</td>
<td>KAl₂Si₃O₈ (240)</td>
<td>2.55 (2.57 [26])</td>
<td>2.64 (2.34° [7])</td>
</tr>
<tr>
<td>Sericite</td>
<td>15120 (10 × 6 × 3)</td>
<td>K₁₂Al₆Si₁₄O₄OH₂</td>
<td>2.82 (2.78 [27])</td>
<td>2.33</td>
</tr>
<tr>
<td>Chlorite</td>
<td>12960 (10 × 6 × 3)</td>
<td>Mg₃Si₂O₇(OH)₄ (250)</td>
<td>2.63 (2.69 [28])</td>
<td>2.15</td>
</tr>
<tr>
<td>Calcite</td>
<td>8910 (9 × 11 × 3)</td>
<td>CaCO₃ (372)</td>
<td>2.73 (2.71 [29])</td>
<td>2.72 (2.69° [9])</td>
</tr>
<tr>
<td>Dolomite</td>
<td>9000</td>
<td>CaMg(CO₃)₂ (372)</td>
<td>2.88 (2.87 [30])</td>
<td>2.86 (2.83° [9])</td>
</tr>
</tbody>
</table>

a The value is converted from cell volume data [9].
b The value is calculated from stiffness tensor [12].
c The value is converted from the results in Ref. [7].

### Table 3

Teter potential parameters of feldspars for X–O interactions, where X = Si, Ca, Al, Mg, Na, Fe, O.

<table>
<thead>
<tr>
<th>Element</th>
<th>Partial charge (e)</th>
<th>A (eV)</th>
<th>r(Å)</th>
<th>C (eV/Å⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>+2.4</td>
<td>13702.91</td>
<td>0.194</td>
<td>54.681</td>
</tr>
<tr>
<td>Ca</td>
<td>+1.2</td>
<td>7747.18</td>
<td>0.253</td>
<td>93.109</td>
</tr>
<tr>
<td>Al</td>
<td>+1.8</td>
<td>12201.42</td>
<td>0.196</td>
<td>31.997</td>
</tr>
<tr>
<td>Na</td>
<td>+0.6</td>
<td>4383.76</td>
<td>0.244</td>
<td>30.700</td>
</tr>
<tr>
<td>K</td>
<td>+0.6</td>
<td>20526.97</td>
<td>0.234</td>
<td>51.489</td>
</tr>
<tr>
<td>O</td>
<td>−1.2</td>
<td>1844.74</td>
<td>0.344</td>
<td>192.580</td>
</tr>
</tbody>
</table>

### Table 4

Potential parameters of carbonate minerals for X–O interactions, where X = Ca, Mg, O, C.

<table>
<thead>
<tr>
<th>Element</th>
<th>Partial charge (e)</th>
<th>A (eV)</th>
<th>r (Å)</th>
<th>C (eV/Å⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>+2.000</td>
<td>3161.634</td>
<td>0.272</td>
<td>0</td>
</tr>
<tr>
<td>Mg</td>
<td>−1.000</td>
<td>3944.861</td>
<td>0.238</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>−1.041</td>
<td>63940.199</td>
<td>0.199</td>
<td>27.899</td>
</tr>
<tr>
<td>C</td>
<td>+1.123</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

As shown in Fig. 1, the simulated densities of the pristine minerals are in good accordance with their experimental data.

### 3.1.2. Normalized density evolution of silicate minerals

Fig. 2 shows the normalized density evolutions of all six silicate minerals as a function of the deposited energy. The densities of silicate minerals exhibit significantly different trends, which may increase or decrease [19]. For albite, anorthite, and microcline, their densities increase slightly with the deposited energy. For quartz, sericite, and chlorite, their densities decrease steeply. It is observed that silicate minerals with similar atomic structure and chemical composition have a similar trend in density variation. Otherwise, the equilibrium density of quartz is reached at higher deposited energy relative to the other silicate minerals.

### 3.1.3. Density and structural evolution of quartz and feldspars

As shown in Fig. 3(a), the density evolution of quartz exhibits a significant decrease trend as a function of the deposited energy, and its final equilibrium density is stabilized at 2.18 g/cm³, which is consistent with the density of 2.20 g/cm³ (maximum RIVE of 17.8%).

![Fig. 1. Comparison between simulated densities and experimental densities of eight pristine minerals.](image1)

![Fig. 2. Normalized density evolution of six silicate minerals at 300 K with respect to the deposited energy.](image2)
observed in the experimental data of quartz upon saturated irradiation [13,18,39,56]. Fig. 3 (b) shows the PDFs of the pristine and irradiated (after saturation) quartz. The pristine quartz exhibits medium-range (>3 Å) and long-range order, while the irradiated quartz exhibit medium-range disorder almost completely. The appearance of the second peak is resulted from the increase in O coordination number of the Si atoms within the irradiated quartz crystal. The significant swelling of irradiated quartz is primarily driven by the disordering of the silicate tetrahedra.

Fig. 4 shows the evolutions of normalized density and the probability of SiIV (four-fold coordinated Si atoms) for quartz at different irradiation temperatures as a function of the deposited energy. Some differences in the densities of the pristine crystal structures occur at different temperatures, while the final densities of the irradiated crystal structures are very close (~2.19 g/cm³). The trends of the probability of SiIV are almost identical until 4.0 eV/atom and vary significantly at moderate deposition energies. Moreover, the saturated fractions of SiIV at a higher deposited energy are similar.

Fig. 5 shows the density evolutions in albite, anorthite, and microcline concerning the deposited energy. The densities of albite, anorthite, and microcline increase to different extents, and their final equilibrium densities are stabilized at 2.66, 2.86, and 2.64 g/cm³, respectively. It is worth noting that albite exhibits a non-monotonic trend of first increase and then decrease. The density evolution of albite simulated by Krishnan et al. [19] is different from the trend in this study, while that of anorthite exhibits a similar trend. The cause of the differences is discussed in section 4.2.
Moreover, these results seem contradictory to the empirical data on the volume change of neutron-irradiated feldspar (about 7–8%) [12], but qualitatively consistent with the density variation upon electron irradiation conducted by Maruyama et al. [57].

Fig. 6 shows the PDFs of the pristine and irradiated albite, anorthite, and microcline. All three feldspars almost completely disorder at medium-range (>3 Å). The peaks of the PDFs at short-range (<3 Å) get lower and wider slightly, which means the topological constraints on short-range atoms become slightly weaker. For anorthite and microcline, the distances of both Si–Si and Al–Al atoms of irradiated crystals change from ~4 Å to ~3 Å, which is consistent with the distance of Si–Al atoms observed in both pristine and irradiated crystals. Meanwhile, the distance reduction of Si–Si atoms of albite is significantly smaller than that of anorthite and microcline. Aggregation of metal cations and collapse of silica networks are observed in irradiated feldspars. In addition, some defects of short-range order appearing in quartz are also observed, such as over-coordinated defects, under-coordinated defects, distorted bond angles, and edge-sharing tetrahedra.

3.1.4. Density and structural evolution of sericite and chlorite

Fig. 7 shows the density evolutions in sericite and chlorite concerning the deposited energy. The densities of both sericite and chlorite exhibit a similar decrease trend with quartz, and their final equilibrium densities are stabilized at 2.33 and 2.15 g/cm³, respectively. The results are consistent with the fact that phyllosilicates exhibit high volume expansions (>15%) at high fluence. In addition, the saturated deposited energies of sericite and chlorite are much less than quartz.

Fig. 6. Pair distribution functions of pristine and irradiated (a) albite, (b) anorthite, and (c) microcline.

Fig. 7. Density evolution in (a) sericite and (b) chlorite with respect to the deposited energy.

3.1.5. Density and structural evolution of calcite and dolomite

Fig. 9 shows the density evolution in calcite and dolomite concerning the deposited energy. The densities of both calcite and dolomite decrease slightly, and their final equilibrium densities are stabilized at 2.71 and 2.87 g/cm³, respectively. The amount of density variation is consistent with the experimental data (<1%) and the previous simulated and experimental results [8,9,22].

Fig. 10 shows the PDFs of the pristine and irradiated calcite and dolomite. The atomic structures of calcite and dolomite are barely affected after irradiation. However, the changes in Ca–O–C and Mg–O–C bond angles observed show the tilting of [CO₃]²⁻ groups. Note that there is no observed bond deformation or decarbonation of [CO₃]²⁻ group, which is modeled as a rigid in this simulation. The distortion and rotation of the [CO₃]²⁻ group alters the atomic packing of the atomic structures, resulting in volume expansion and density reduction of the calcite and dolomite [9]. Lattice growth and radiation-induced disorder observed in post-irradiated calcite and dolomite samples agree well with these simulated results [9,58,59].
3.2. Elastic properties evolution of aggregate-forming minerals

The elastic moduli at different directions for each mineral were calculated by LAMMPS, expressed by the $6 \times 6$ stiffness tensor matrix. As a whole, the elastic tensors of all silicate minerals eventually exhibit isotropic after irradiation, while the elastic tensors of the irradiated carbonate minerals remain anisotropic. Note that natural minerals exist mainly as polycrystalline in aggregates, hence the Voigt-Reuss-Hill [60] approximation was used herein to estimate the average elastic moduli of the equivalent random-oriented polycrystalline minerals. As shown in Fig. 11, the final elastic modulus ratio versus density ratio (final irradiated state to pristine state) is compared with the density–modulus scaling obtained by Krishnan et al. [48]. The results of all eight minerals are roughly following this relationship. The elastic modulus of quartz degrades significantly after irradiation, which is consistent with the experimental results under 3 MeV Si-ion irradiation [61]. The degradation of elastic modulus for sericite and chlorite is similar to that of quartz, while the degradation of elastic modulus for feldspars and carbonate minerals is relatively small. Noted that the elastic modulus ratio changes in the opposite direction with the density ratio for albite and microcline, but in quite small magnitudes. Furthermore, to examine the degradation mode of minerals’ elastic moduli with the deposited energy, the elastic modulus ratio versus density ratio of
and the healing process reduces the number of point defects at high temperatures. The over-coordinated and the under-coordinated atoms adjust their coordination number to become normal. According to the previous studies [17,62,63], the structural changes in irradiated quartz at 300K occur in three stages concerning the deposited energy, including the growth stage of over-coordination and under-coordination defects (<4.0 eV/atom), the growth stage of large void defects, and the equilibrium stage of large void defects [17]. Moreover, the damage-healing mechanism for the pristine quartz is dominated by the local relaxation mechanism at 300 K and by the chain-hopping mechanism at 700 K and 1400 K [20]. The atomic structure of quartz still has a large crystallinity and the topological constraints are strong enough during the first stage [17], hence the temperature effect is weak. During the second stage, large voids (>7 Å) surrounded by unstable atomic structures appear at random positions, and the density of quartz continues to decrease until a plateau is reached due to the balance between the generation and annihilation of large voids [17]. At this stage, the self-adjustment of the atomic structure and the elimination of internal imbalance forces are easier. Therefore, the recombination and healing of defects during the cooling of cascade damage are evident at high temperatures by the local relaxation mechanism. Nevertheless, we believe that the density change at the second stage is controlled by the generation of large voids, hence the damage-healing phenomena at higher deposition energies have no significant effect on density.

4.2. Effect of Na–K–Ca substitution on feldspars RIVE

The distance reduction of Si–Si atoms in albite is significantly smaller than that of anorthite and microcline, and stabilizes at the deposited energy of 3.0 eV/atom with a small collapse of the Si network. The decrease in density above the deposited energy is primarily caused by the disordering of the silicate tetrahedra. Consequently, the density of albite increases and then decreases in this study. However, the density of albite continues to decrease in the results simulated by Krishnan et al. [19] since the distance of Si–Si atoms does not change. The cause of the differences is that the value of 1844.74 eV instead of 2029.22 eV was used as the parameter A for O–O interaction in this study. The PDFs of the pristine albite in the two cases vary slightly, though minor differences in terms of Si–O bond length and coordination number for silicon and other cations [43]. Nevertheless, the pristine densities of feldspars were predicted more accurately in this study. The lattice constants of albite also show extension or contraction at different crystal axes in the irradiation experiment [7]. Therefore, we believe that the force field is reasonable for describing the pristine and disordered structures of feldspars, but may not be accurate enough for predicting the cumulative damage progress of irradiated albite. Other force fields should be considered to confirm the changes of albite in the future. For anorthite and microcline, the distance of Si–Si atoms decreases considerably, which causes a continuous increase in density. The effect of Na–K–Ca substitution on feldspars RIVE exhibits a correlation with the size of the metal cation in this study. The cations of albite, microcline, and anorthite initially exist in the channels between the Si (or Al) networks, and they are bonded to the Si network with ionic bonds. Ionic bonds have lower bond energies and weaker orientations than covalent bonds [64]. Therefore, the cations are more easily accelerated to other random locations by the PKA (or SKA) and then reorganized to eliminate the unbalanced forces in the atomic structure. Numerous cations leave their initial positions and accumulate, leading to the collapse of the silica network structure. We believe that the size of the cations in the feldspars determines the extent of their Si network structural collapse after irradiation.
The current empirical model assumes that the maximum RIVE of feldspars is independent of chemical composition, with a maximum volume expansion (~7%–8%) [8]. However, the volumes of all three feldspars exhibit a reduction to different extents in this study. The reasons for the discrepancy between the simulations and experimental data can be: (1) the irradiated experimental feldspar samples are generally not single-crystal samples, but natural feldspars of mixed crystals (i.e., homogeneous mixtures of analogs) of An-Ab-Or composition, and even contain highly expanded mineral types such as quartz [61]; (2) The crack volume of irradiated feldspars may control its volume expansion compared to the changes in lattice parameters [8]. The irradiated feldspar was observed under the microscope as if it was densely pelletized [65] and the feldspar minerals were cracked and partially dispersed under neutron irradiation (especially at higher neutron fluence). Therefore, the maximum RIVE value of 7–8% suggested in the literature includes the amount of crack volume within the mineral. Nevertheless, the simulations of representative feldspars show that single crystals shrink to some extent depending on the size of their cations upon irradiation, which could provide a better understanding of the cracking behavior of natural feldspars.

4.3. Maximum RIVEs of phyllosilicates

The volume of sericite and chlorite appears a high expansion (~18%) at the lower deposited energy (~6.0 eV/atom) in this study, though the degree of polymerization of the [SiO4]4+ tetrahedra of sericite and chlorite is smaller than that of quartz and feldspars. Among the available experimental data of phyllosilicates, a couple of data for muscovite show high volume expansions (>15%) for the fluence above 1.5 nE > 10 keV·pm−2, while the remaining data does not exhibit an expansion higher than 5% for fluences below 1.25 nE > 10 keV·pm−2 [7]. The volume expansion of muscovite is lower than that of sericite in this study. Note that the irradiation experiment may not continue until saturation, which means the experimental data may underestimate the expansion potential of muscovite. Moreover, we observe that the coordination number of Al (or Mg) atoms in irradiated sericite and chlorite decreases from six-fold to four-fold, which is the preferred coordination state with low packing efficiency for Al atoms [66]. Similarly, the decreased coordination number of Al (or Fe) atoms in irradiated jadeite (NaAlSi2O6) and almandine (Fe3Al2Si3O12) is also observed in previous simulations, and they both exhibit larger volume expansions (~19%) than the other minerals at a lower deposited energy [19]. Therefore, we believe that the apparent sudden increase of RIVE in muscovite is caused by the decreased coordination number of Al atoms, and the presence of non-optimally coordinated atoms is an important factor affecting the volume expansion potential of similar minerals.

4.4. Elastic modulus evolution of irradiated minerals with respect to neutron fluence

In this study, the elastic modulus ratio versus density ratio of quartz at different deposited energies is following the density—modulus scaling. It should be noted that the disordering progress is directly caused by the repeatedly accelerated PKA with 600 eV in section 2.2, rather than by the directly scattered neutrons in the reality. Therefore, the relationship between mineral density (or volume) versus deposited energy is difficult to translate into mineral volume versus neutron fluence [14]. However, the relationship between elastic modulus versus density can reflect the degradation of the elastic properties caused by the “nano-voids” within the mineral during irradiation. Furthermore, based on the law of mineral volume versus irradiation conditions obtained through irradiation experimental data [8], it provides an idea to predict the degradation of the elastic modulus of minerals under different irradiation conditions.

5. Conclusions

In this paper, the densities and elastic moduli of eight typical aggregate-forming minerals in concrete under neutron irradiation were simulated by molecular dynamics. The results could further provide the basis for predicting the volume and elastic properties of irradiated aggregates based on the component minerals. The main conclusions obtained are as follows:

(1) The densities of aggregate-forming minerals vary differently with the deposited energy, while minerals with similar atomic structure and chemical composition have a similar trend in density variation due to the similar amorphization mechanism. Meanwhile, the densities of silicate minerals are more affected by irradiation than those of carbonate minerals.

(2) The damage-healing phenomena in the cumulative damage progression of quartz are pronounced at moderate deposition energies under 513 K, while they have no significant effect on density. The effect of Na–K–Ca substitution on feldspars RIVE exhibits a correlation with the size of the metal cations within their crystals. The significant swelling of irradiated sericite and chlorite is mainly motivated by the decreased coordination number of Al (or Mg) atoms.

(3) The elastic tensors of all silicate minerals are almost isotropic after irradiation, while those of irradiated carbonate minerals remain anisotropic. Moreover, the elastic modulus ratio versus density ratio of eight minerals at saturated deposited energy is roughly following the density—modulus scaling relationship.

CRediT authorship contribution statement

Weiping Zhang: Conceptualization, Writing – review & editing, Resources, Supervision. Hui Liu: Conceptualization, Methodology, Formal analysis, Writing – original draft, Visualization. Yong Zhou*: Conceptualization, Writing – review & editing, Supervision. Kaixing Liao*: Funding acquisition, Methodology, Project administration. Ying Huang: Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors sincerely thank the anonymous reviewers for their thorough reviews and constructive comments and the editors for their selfless contributions in the manuscript processing.

References


[3] Y. Le Pape, Structural effects of radiation-induced volumetric expansion on


