Mechanisms behind radiation-induced deterioration of concrete

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Abstract. This paper describes the mechanism of radiation-induced deterioration of concrete and its components based on the literature review. The deterioration mechanism in different levels starting from the interaction between neutron and nucleus through the mineral metamictization and cement paste shrinkage up to the reduction of mechanical properties of concrete is explained in detail. All basic dependencies and patterns of volumetric change of minerals, aggregates, cement paste and finally concrete are also described in order to create a base for the future development of numerical models. Finally, the reduction of concrete mechanical properties is in correlation with its volumetric expansion. The radiation-induced volumetric expansion of concrete is affected by irradiation conditions (neutron fluence, neutron spectrum and temperature) and concrete composition (the amount, the proportion, the type and the structure of the minerals in the aggregate composition and the amount, the composition, the age and the structure of the cement paste).

1. Introduction
According to The World Nuclear Industry Status Report [1], the unit-weighted average age of the world operating nuclear reactors is rising continuously, and by mid-2017 stood at 29.3 years, up from 29.0 a year ago and 28.8 two years ago [2]. Despite the fact that the initial design operating period of nuclear power plants is 30 to 40 years, over a half of the total 234 units have operated for 31 years and more, including 64 that have run for 41 years and more. This means that the nuclear power plants which are nearing the end of their licensed operating period need to be either shut down or their operation time licenses have to be prolonged. The license renewal is preferable before the reactor shutdown because of the long nuclear power plant decommissioning process which is also associated with significant costs. For example, 84 of the 99 operating U.S. units had received a license extension with a further nine applications under review as of 1 July 2017.

The long-term exposure to radiation can cause the damage in the construction materials. Since the biological shield of the nuclear power plants most often consists of concrete, the possible damage of concrete due to radiation is of particular interest. In order to predict the damage of concrete and create a comprehensive numerical model, it is necessary to understand the mechanism of concrete deterioration and identify the main relations and patterns.

The research presented in this study is focused on review of the available literature in order to identify the main dependencies in the field of the effect of radiation on concrete for the future numerical modelling.
2. Deterioration mechanism

2.1. Neutron irradiation

Interaction of neutrons with matters occurs through inelastic scattering, elastic scattering and absorption depending on the neutron energy. The fast neutrons are scattered inelastically. When a high-energy fast neutron collides with a nucleus, it is absorbed and the compound nucleus is created. The compound nucleus decays into a lower-energy neutron and an excited nucleus. The nucleus gives up excitation energy by emitting one or more gamma rays (so-called secondary gamma-ray). The traveling direction of both, the neutron and the nucleus, are changed after collision. This process may repeat until the fast neutron becomes an intermediate neutron. It should be noted that inelastic scattering is typical for neutron collision with heavier atomic nuclei. The intermediate neutrons are scattered elastically. After intermediate neutron collision with the nucleus, its energy is transferred to the recoiling nucleus and both, the neutron and the nucleus, change their traveling direction, but the intermediate neutron does not have enough energy to cause the nucleus excitation and the subsequent gamma-ray release. The elastic collisions may repeat until the intermediate neutron becomes the thermal neutron. When the thermal neutron collides with the nucleus, its energy is too low to cause further scattering and its energy is absorbed in the collision.

Concrete is a composite material which consists of cement paste, aggregates (fine and coarse) and water, while in turn the aggregates are composed of minerals. The high energy neutrons cause defects in the lattice structure of the minerals by the elastic scattering and the inelastic scattering. According to [3], the threshold energy of the neutrons to cause the defects in the lattice structure of the minerals is equal to 10 keV. A vacancy at the original site and an interstitial defect at the new location (Frenkel pair) are created due to the neutron ballistic effect. These point defects can be accumulated and result in mineral metamictization (amorphization in some literature) which leads to the significant change in the properties of minerals (volume, density etc.) and consequently changes the properties of concrete (volume, strength, elastic modulus etc.). It is believed that the effect of the neutron irradiation on the cement paste is much smaller in comparison with the minerals and the aggregates and rather results in the cement paste shrinkage, because the calcium silicate hydrate (C-S-H) gel, the main component of cement paste, is amorphous and has very porous structure. The pore volume represents about 20 % of C-S-H volume. The threshold energy of the neutrons to cause the damage to the cement paste is much higher and equal to 0.8 MeV. However, [3] discusses the Portlandite metamictization due to the neutron irradiation and its subsequent reaction with the carbon dioxide presented in air. This leads to CaCO3 formation (carbonation reaction), which can affect the properties of the cement paste. It should be noted that the high-energy neutrons may also excite water and thus provoke the radiation-induced water decomposition (radiolysis) with the consequent drying due to the gas release, which may mainly vary the properties of the cement paste since the aggregates have a much lower amount of water in their composition.

According to [3], the contraction of the lattice structure of the minerals due to the creation of the vacancy is lower than the lattice structure expansion due to the interstitial defects, see Figure 1, therefore the mineral metamictization due to the accumulation of the defects causes the radiation-induced volumetric expansion (RIVE). An uneven expansion of the different minerals in the aggregates causes concentration of stresses. When the stresses exceeds the strength of the material the cracks start to develop. Moreover, the cement paste may shrink under the exposure to neutron irradiation due to the radiation-induced water evaporation which in combination with the aggregate expansion causes development of cracks in the cement paste. The crack propagation in the aggregates and the cement paste leads to reduction of the elastic modulus and the compressive and tensile strength of concrete. Thus, the volume change of the aggregates and the cement paste can be considered as the primary factor of the radiation-induced damage of concrete.

The effect of neutron irradiation on creep of concrete is not yet understood. In the study presented in [4], the influence of neutron irradiation on concrete creep was studied and it appeared to be insignificant, nevertheless, the final conclusion is difficult to draw from this experiment. According to [3], the creep
of the irradiated samples is approximately seven times higher in comparison with the control samples, however an increase in the creep is explained by the high temperature (240 °C) which accompanied irradiation in the test reactor. The research presented in [5] also concludes that the increase in the creep is equivalent to its increase under the elevated temperature.

2.2. Gamma-ray irradiation
The gamma-rays emitted during the inelastic neutron scattering cause the electron excitation and subsequently remove electrons from the atoms by the electron-positron pair production, the Compton scattering and the photoelectric effect that may also cause the water radiolysis, which leads to drying due to gas release [6]. The radiolysis is accompanied by the free radicals and hydrogen peroxide formation [7, 8], which may react with cement hydration products and may alter the cement paste properties and even provoke the carbonation reaction [9-11]. Finally, the gamma-ray is absorbed by the material as the thermal atom vibration, which causes the so-called gamma heating which can also affect the cement paste properties. The neutron radiation is always accompanied by the gamma-rays and thus also with an increase in temperature.

The effect of the neutron irradiation and the gamma irradiation on water can differ due to the difference in the transmitted to water energy during the interaction, [12].

It is believed that the gamma-rays affect only slightly the aggregate properties and that majority of the changes appear in the cement paste. According to [13], a significant reduction of the cement paste properties appears beyond the threshold of 200 MGy of the absorbed gamma-ray dose. Also, in [14] the hydrates decomposition within the absorbed gamma-ray dose range of 130 to 836 MGy can be found. On the other hand, the reduction in compressive strength at much lower absorbed gamma-ray dose (15 % reduction with the absorbed dose of 22 MGy and 10 % reduction with the absorbed dose of 0.3-0.5 MGy, respectively) was observed in [15-16]. However, the mechanism of this strength reduction is still unclear. According to [10] the strength of cement paste reduces due to its drying and heating under the gamma rays while the radiation-induced carbonation increases the strength of the cement paste, [11].

According to the only one available research of the effect of gamma-ray irradiation on the creep of the cement paste presented in [17], the gamma-ray reduces the creep and increases the autogenous shrinkage. However, the mechanism of this process is also not fully understood and demands additional experimental investigation.

3. Main patterns in radiation-induced volumetric changes

3.1. Minerals
The RIVE of the minerals, first of all, depends on the neutron fluence which is the accumulated number of the neutrons travelling through the unit area and also can be defined as the neutron flux integrated over the time period. The threshold fluence to cause the RIVE of minerals is in the order of $10^{19}$ n/cm$^2$. However, the neutron fluence by itself can not characterize the RIVE, since the same amount of the neutrons can cause different damage, because the high-energy neutrons can create more than one Frenkel pairs and cause the cascade of the lattice defects. Therefore, the RIVE depends not only on the neutron
fluence but on the energy spectrum of the neutrons. With the same fluence the hard neutron spectrum (the spectrum with a higher amount of high energy neutrons) causes more lattice defects and consequently higher RIVE than the soft neutron spectrum (the spectrum with a lower amount of high energy neutrons), see Figure 2. The number of point lattice defects can be predicted by, for example, Kinchin-Pease model, [18].

![Figure 2](image_url)  
**Figure 2.** Comparison of RIVE due to hard neutron spectrum and soft neutron spectrum: a) neutron irradiation spectrum, b) RIVE, [5].

The number of lattice defects also depends on the temperature during irradiation. With higher temperature, the probability of the lattice defects recombination is higher, so some lattice defects can be annihilated. Therefore, the higher temperature results in lower RIVE, see Figure 3. However, the normal operation temperature of nuclear power plant is about 60 °C, which corresponds to relatively high RIVE. The silicate minerals are the most sensitive to the elevated temperature, see Figure 3(b) while the effect of elevated temperature on RIVE of carbonates is insignificant in the temperature range of 30-270 °C, [3].

![Figure 3](image_url)  
**Figure 3.** Influence of temperature on RIVE of α-quartz: a) RIVE versus temperature at different fluence [3], b) RIVE versus neutron fluence at different temperature [5].

The RIVE also depends on the type and the structure of the minerals. The highest RIVE is typical for the framework silicates (Tectosilicates) with the highest amount of silica and is equal to 17.9 % for quartz, [3]. The RIVE reduces with the decrease in the silica content up to 8 % for alkali-feldspar, [3]. Also the RIVE reduces with the decrease in the silicate degree of polymerization from the framework silicates to the sheet silicates (Phylosilicates), the RIVE is up to 5 % for mica, [3], and further to the
chain silicates (Inosilicates), the RIVE of double-chain silicates is about 2.8 % and the RIVE of single-chain silicates is about 1.5 %, [3], and finally for the island silicates (Nesosilicates), the RIVE of olivine is about 0.9 % [3], see Figure 4.

![Figure 4. Influence of mineral structure on RIVE of silicates, [5].](image_url)

The RIVE of the carbonates is typically much lower in comparison with the silicates and varies in the range of 0.5-4 %. The higher RIVE occurs in carbonates with complex composition and the lower structure symmetry, [3].

Moreover, according to [3], the RIVE depends on the heat of fusion of the minerals, which characterizes the energy required by the mineral for phase transformation, while according to [19], the RIVE depends on the bond-dissociation energy of the minerals, which characterizes the energy needed for chemical bond dissociation. Basically, these two parameters describe how strong and stable a lattice structure is, however, they affect the RIVE in the opposite way. With lower heat of fusion and/or with higher bond-dissociation energy, the RIVE becomes higher.

From the above, the following patterns can be highlighted:
The RIVE of mineral is higher with:
- Higher neutron fluence
- Harder neutron spectrum
- Lower temperature
- Higher silicate degree of polymerization (for silicates)
- Higher silica content (for silicates)
- More complex composition (for carbonates)
- Lower structure symmetry (for carbonates)
- Lower heat of fusion and/or higher bond-dissociation energy

### 3.2. Aggregates
The RIVE of aggregates is defined by the minerals present in their composition and depends on the amount of the minerals with the highest RIVE, see Figure 5. The complex stress state due to the different level of the RIVE of the minerals results in development of cracks, therefore, the RIVE of aggregates is higher than the RIVE (up to 20-23 %) of the minerals due to additional volume of cracks. Also, the RIVE of coarse-grain aggregates is usually higher that the RIVE of fine-grain aggregates, [3, 5].
The amount of the amorphous material also affects the RIVE of the aggregates since the amorphous materials, such as glass, contract under exposure to irradiation, [3, 5], and can reduce the aggregate RIVE.

Therefore, the RIVE of aggregates depends on
- Mineral composition of the aggregates
- RIVE of the minerals
- Grain size of the aggregates
- Amount of amorphous material

The reduction of the aggregates mechanical properties (strength, elastic modulus, etc.) correlates with their RIVE and the volume of cracks.

3.3. Cement paste
The Portland cement is the most commonly used type of cement and so the available experimental data are predominantly focused on the Portland cement.

The amorphous C-S-H gel is the main component of cement paste, therefore, instead of the typical magnitude of RIVE for crystalline materials, contraction of the cement paste (up to 9.5 % by volume at 400 °C, [3]) under irradiation is observed. The reason of the cement paste contraction is in the hydrate decomposition and the water radiolysis which leads to the loss of water and is accompanied by release of a significant amount of gas. The correlation between the cement paste shrinkage and the loss of water can be observed. According to [3], the cement paste can lose up to 64 % of water (included chemically combined and adsorbed water).

Similarly to the minerals, the effect of radiation on the cement paste increases with the increase in the neutron fluence and with the harder neutron spectrum. However, temperature has an opposite effect than in the case of minerals. The radiation-induced shrinkage of the cement paste is higher with higher temperature due to the water evaporation, see Figure 6 a).

The radiation-induced shrinkage of the cement paste reduces with an increase in the water-to-cement ratio due to the increase in carbonation. The carbonates fill in the pores and restrict the cement paste contraction. However, the early-age cement paste shrinks more than the hardened cement paste under exposure to neutron irradiation and its shrinkage increases with the increase in the water-to-cement ratio, [3].

It is believed that admixture and additives can vary the cement paste response to the neutron irradiation.

From the above we can conclude that the radiation-induced shrinkage of cement paste depends on:
- Neutron fluence
- Neutron spectrum
- Temperature
- Water-to-cement ratio
- Age of cement paste
- Presence of admixtures or additives

According to [5], the strength of cement paste reduces up to 40% and according to [3] the strength reduction can reach 72%, see Figure 6 b). The strength of the early-age cement paste may increase up to 45% at the beginning of irradiation and then reduces up to 37%.

![Figure 6](image)

**Figure 6.** Radiation-induced changes in hardened cement paste: a) volume change, b) strength change, [3].

### 3.4. Concrete

The volumetric change of concrete depends on the volumetric change of the cement paste and the aggregates and its proportion in the concrete. The parameters on which the volumetric change of concrete depends can be divided into two groups:

- Irradiation conditions (neutron fluence, neutron spectrum and temperature)
- Concrete composition (amount, proportion, type and structure of minerals in the aggregates and amount, composition, age and structure of the cement paste)

The volumetric expansion of the concrete due to the neutron irradiation leads to reduction of strength and modulus of elastic due to the crack formation and the aggregate and the cement paste strength reduction, see Figure 7. The volumetric expansion of concrete is in correlation with reduction of its mechanical properties.

![Figure 7](image)

**Figure 7.** Reduction of mechanical properties of concrete with different composition: a) strength, b) elastic modulus, [3].
4. Conclusions
The mechanism of the radiation-induced deterioration of concrete and its components is described in detail based on the literature review.

All the basic dependencies and patterns of the volumetric change of minerals, aggregates, cement paste and concrete are also described.

The radiation-induced volumetric expansion of minerals is affected by neutron fluence, neutron spectrum, temperature, silicate degree of polymerization (for silicates), silica content (for silicates), complexity of composition (for carbonates), structure symmetry (for carbonates) and heat of fusion and/or bond-dissociation energy.

The radiation-induced volumetric expansion of aggregates is affected by mineral composition of the aggregates, the radiation-induced volumetric expansion of the minerals, grain size of the aggregates and amount of the amorphous material.

The radiation-induced shrinkage of the cement paste is affected by neutron fluence, neutron spectrum, temperature, water-to-cement ratio, age of the cement paste and presence of admixtures and additives.

Finally, the radiation-induced volumetric expansion of concrete is affected by irradiation conditions (neutron fluence, neutron spectrum and temperature) and concrete composition (amount, proportion, type and structure of minerals in the aggregate composition and amount, composition, age and structure of the cement paste).

The reduction of the concrete mechanical properties is in correlation with its volumetric expansion.

It is believed that this study can help to create a base for future development of related numerical models.

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