Volume expansion of quartz aggregate in ion-irradiated concrete

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Quartz aggregate in concrete irradiated by Si-ions with a fluence of $5{\cdot}10^{14}$ ions/cm^2 at 300 keV exhibited an out-of-plane expansion of ~ 80 nm.

Quartz is the primary mineral component of most concretes and exhibits the highest neutron radiation-induced volume expansion (i.e. 17.8 %) of all minerals yet examined.[1] The volume expansion is due to structural relaxation that occurs when a critical concentration of defects (E′ centers) has been produced by the interaction of the radiation imparted to the crystal lattice.[2] The mechanism of this amorphization process appears to be indifferent to the type of radiation (i.e. neutrons, electrons, ions, and photons, e.g. gamma). The chemical durability of concrete is largely dependent on the reactivity of the silicate aggregates to alkaline pore water, which ultimately results in the alkali-silica-reaction. The rate-determining step for the dissolution of quartz is associated with $Q^4 \rightarrow Q^3$, which is considerably slower relative to the subsequent dissolution steps $Q^n \rightarrow Q^{n-1}$, where the Q^n nomenclature represents the Si-tetrahedron with n being the number of Si-atoms the tetrahedron is bound to.[3] As quartz amorphizes due to radiation, the concentration of Q^3 species increases. The ultimate goal of this work is to examine how radiation-induced changes in quartz effects dissolution behavior in alkaline media and to resolve (spatially and temporally) the influences of grain boundaries, defects, crystal strain, and Q^3 content. In this paper we examine the volume change of quartz.

EXPERIMENTAL. Non-radioactive concrete (ca. 48 years old) from the dome section of a reactor pressure vessel forming the base of the reactor was acquired during the dismantling of a decommissioned nuclear power plant, Stade, in Hamburg, Germany. Two slices (ca. 5 mm thick) of concrete from a drill core were obtained using a diamond-coated and water-cooled circular saw. Four polished sections with a diameter of 3 cm were prepared by vacuum impregnation using a two-component epoxy-based resin (Araldite 2020). The samples were ground smooth using SiC paste with a final diamond polish (3 µm). Mineralogical composition of the aggregates was identified *in situ* by µ-Raman spectroscopy (HORIBA Jobin Yvon LabRAM Aramis Vis) using a laser with wavelength 532 nm. Aluminium foil was placed on each polished section so as to respectively protect and expose parts of the aggregate to radiation. Si-ion irradiation with a fluence of $5{\cdot}10^{14}$ ions/cm^2 at 300 keV was conducted under vacuum at room temperature without cooling. Some sputtering could be observed on the samples after irradiation. Depth profiles of the irradiated samples were examined by Vertical Scanning Interferometry (VSI) and Confocal Microscopy using a S Neox 3D Optical Profiler (Sensofar Metrology).

RESULTS. The minerals making up the aggregate were clearly identified by µ-Raman spectroscopy to be α-quartz and potassium feldspar (microcline: $KAlSi_3O_8$), the latter always intergrown with quartz. The results are illustrated in Figure 1. The most significant depth profile change observed in the sample is the ablation of the epoxy resin (- 600 nm). The volume change in quartz is observed as an increase in height of 80 nm. Taking into account an ion-penetration depth of 429 nm (estimated in the Kinchin-Pease calculation by SRIM)[4] for pure quartz, the volume expansion amounts to 15.7 %. No observable difference in average height between radiated and non-radiated areas on the black aggregate containing feldspar could be ascertained. Aggregates containing feldspar were generally found to display a rougher surface than aggregates containing only quartz. The maximum volume expansion observed for potassium feldspar has been reported to be 7.7 %.[1] Considering the same extent of radiation damage as observed for the quartz aggregate in this work, and a calculated ion-penetration depth for $KAlSi_3O_8$ (estimated by SRIM) of 604 nm, a height increase in microcline of ~ 41 nm is expected. The troughs that the rougher surface of microcline exhibits could accommodate the expansion laterally in the plane, which decreases the expected out-of-plane expansion to ~ 3.4 nm, which is close to the resolution for VSI (1-2 nm). In addition, curvature of granular surfaces deflects light, which inhibits VSI measurements. Finer surface polishing of the specimen is therefore required in order to accurately observe radiation-induced volume expansion of microcline.

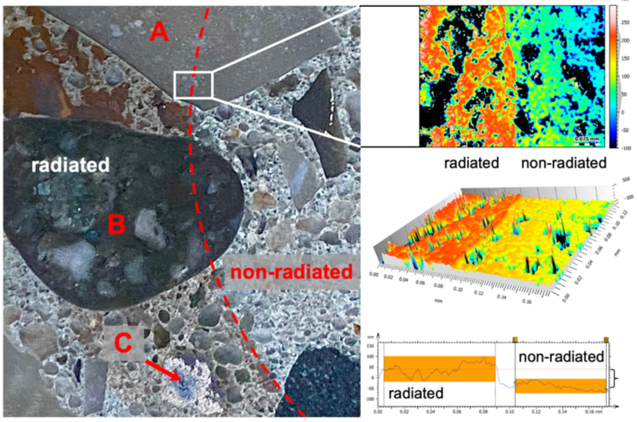

Fig. 1: Image showing radiated area (epoxy resin tarnished brown) left of the red dashed line and non-radiated area (epoxy resin clear) right of the dashed red line. Area of interest (AOI) in the white square depicting the boundary between radiated and non-radiated regions on large quartz aggregate. A = quartz (SiO_2), B = feldspar (microcline: $KAlSi_3O_8$), C = sputtering from Si-ion irradiation. VSI of AOI indicating depth profile, exhibiting +80 nm on quartz, -600 nm on epoxy resin, and unspecified on feldspar.

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