Stress-relaxation of crystalline alkali-silica reaction products: Characterization by micro- and nanoindentation and simplified modeling

Chi Zhang [a], Luca Sorelli [a,*], Benoît Fournier [b], Josée Duchesne [b], Josée Bastien [a], Zhao Chen [a]

[a] Université Laval, Civil and Water Engineering Department, 1065 avenue de la medecine, G1V0A6 Quebec, Canada
[b] Université Laval, Geology and Geological Engineering Department, 1065 avenue de la medecine, G1V0A6 Quebec, Canada

HIGHLIGHTS

- Microindentation test allowed assessing the relaxation behaviour of crystalline *in-situ* ASR products.
- The ASR viscous behaviour showed a twofold mechanism possibly related to water movements and interface slips.
- Nano-indention seems to have characterized the behaviour of few ASR plate-like crystals.
- The smaller the scale, the more higher are the apparent visco-elastic properties of ASR products.

ARTICLE INFO

ABSTRACT

Alkali-silica reaction (ASR) is a major issue for the durability of concrete structures worldwide. Fostering recent microindentation works on the elastic property of ASR products, this work aims at further characterizing their viscous property. In particular, this study focuses on the relaxation behaviour of ASR crystalline products which are preferentially formed within cracks at the center of the reactive aggregates in real field concrete structures. First, the surface roughness and the chemical composition of ASR products were examined by Scanning Electron Scanning (SEM) and Energy Dispersive X-ray spectroscopy (EDS). Finally, the viscous behaviour of crystalline ASR products was characterized by performing load-relaxation tests by microindentation, providing new knowledge on the relaxation behaviour of the ASR crystalline products which was about 40%. Furthermore, nanoindentation test were also carried out to better understand the possible length-scale effect. In spite of the large scatter, the characterization at lower scale by nanoindentation showed that the ASR rosette crystals have a greater modulus and lower relaxation rate. This is likely due to the fact that the volume probed by nanoindentation is close to the size of ASR crystals and related interfaces. Finally, a simplified rheological model was employed to estimate the viscosity and characteristic time of the ASR crystalline products. The present result provide new knowledge on the viscous behaviour ASR products which can be helpful for better understanding ASR products and improve existing multiscale models.

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1. Introduction

Expansion due to Alkali-Silica Reaction (ASR) is a major durability issue for civil engineering structures, such as bridges, pavements, dams, etc. [4,14,17,61]. Although ASR was first reported in 1940 [59,60], its reaction-expansion mechanism is rather complex and not yet fully understood [20,50]. Amorphous and metastable forms of silica, as well as microcrystalline and strained forms of quartz present in certain aggregates, are attacked by the hydroxyl ions present in the pore solution, causing their dissolution to form silicate ions. The latter react with alkalis and calcium ions present in concrete pore solution, precipitating into hydrous alkali-calcium-silica gel of variable stoichiometry, molar volume and mechanical properties [14,27,45]. ASR gels have a general composition of $(SiO_2)\cdot(Na_2O)_n\cdot(K_2O)_k\cdot(CaO)_c\cdot(H_2O)_x$ and can be rewritten using cement chemistry notation as N–C–S–H, where N represents alkali oxides. In addition, a small concentration of Mg may be present as a substitution for Ca [69]. ASR products often exhibit a layered structure hinting to a periodical sol/gel transformation induced by swelling and drying [17]. Several authors observed that ASR products exhibited a rosette-like (or

* Corresponding author.
  E-mail address: luca.sorelli@gci.ulaval.ca (L. Sorelli).

plate-like) micro-texture in cracks located in the center of reactive aggregate particles, while they are more amorphous in the crack zone close to the edge of the aggregate particle [7,20,28]. The latter have a higher calcium content up-taken from the surrounding cement paste [24,28,58]. Other kinds of ASR products have been reported in the literature, e.g. hummocky and/or stratified/recrystallized gel, alveolar micro-texture, and also coexistence with ettringite has been found, e.g., a hydrous calcium aluminium sulfate mineral [7,20,26,45].

The ASR gel has the capacity to imbibe water molecules causing extensive swelling. Once the increase of ASR volume is constrained, internal pressure increases up to the cracking of the aggregate particle [6,54,61,62]. The cracks develop in the reactive aggregate particles first at lower expansion levels (i.e.: inferior than 0.05%) and then extend into the cement paste as the ASR reaction/expansion progresses [6,51,55,63]. The engendered internal pressure can be released due to the viscous behaviour of the ASR gel, which can permeate the surrounding porous zones and cement matrix [23]. Thus, the pressure build-up depends on the ASR volume increase, the elastic properties of the aggregate, the permeability of the matrix and aggregate to the ASR migration, and the ASR rheological properties [69]. At the macroscopic scale, concrete expansion depends on the ASR reaction extent, the particle size and volume content of aggregates, the local stress/restraint situation, and the anisotropic growth of cracks [22,34,36].

As for a modeling standpoint, a large number of multi-scale models have been developed to consider specific aspects, such as: ASR reaction kinetics, alkali diffusion, moisture content, aggregate particle size distribution, damage and expansion generation in concrete [5,18,21,25,29,36,41,42,44,49,48,56,64]. Interestingly, a chemo-physico-mechanical approach was developed to take into account the transport and mechanical properties of ASR products and explain the pessimum size effect [23]. In particular, discrete modeling has been recently developed to account for mechanisms at stake at the microstructure scale, such as: anisotropic crack growth [3] or the gel growth in aggregate pockets [6,12,70]. Due to lack of experimental data, such models consider only the elastic properties of the ASR products, but the visco-elastic nature of the ASR products is ignored.

In spite of advancements in modeling ASR damaged concrete, very few data are available in open literature on the mechanical property ASR products. For instance, the E-modulus of synthesized silica gel was estimated to vary from 11 GPa to 35 GPa, depending on the calcium content [37,46]. Recently, a microindentation technique has been successfully applied to characterize the properties of *in-situ* ASR products [28]. Their results showed that the ASR products located in the crack at the center of the aggregate, which are preferentially plate-like crystals (e.g., rosette-like structure, are characterized by an E-modulus and Vickers of about 5–10 GPa and 10–20 MPa, respectively. Instead, the ASR products close to the edge of the aggregate particle, which have more amorphous structure, exhibited higher E-modulus and Vickers hardness with values up to 45 GPa and 270 MPa, respectively. Although their results measured substantial creep of the ASR products, no measurements were attempted.

This work aims at further applying indentation techniques for fully characterizing the viscous relaxation behaviour of ASR products, especially for those with crystalline-like structures which are commonly found in the cracks inside the reactive aggregate particles. The research significance of this work is the characterization of the relaxation behaviour of ASR crystalline products and the quantification of their visco-elastic properties by a simplified analysis. The present results provide first estimates the viscosity of ASR products, which may be helpful for discerning different ASR products [24,27], for better understanding the structure the effect of the atomistic structure of alkali silicate gels on its mechanical proper-

ties [30], for improving advanced modeling in the migration of ASR products and the build-up pressure in the aggregate or the migration of ASR products along crack channels under high pressure head [3,11,35].

2. Materials and methods

2.1. Material and sample preparation

Cores, 100 by 225 mm in size, were extracted from an ASR-affected concrete pavement that was built in the 1970's in the Bécancour area (Québec, Canada). The two-lane pavement, which has never been opened to traffic, is composed of 15 m long sections that are linked by dowel bars. No records could be found of the specific mix design of the original concrete; however, the main Quebec DOT specification at the time was requesting a compressive strength of about 31 MPa at 28 days for this type of application.

The concrete incorporated a highly-reactive siliceous limestone from the Neuville formation (St. Casimir member) exploited in the Trois-Rivières area across the St. Lawrence River [15]. The pavement section, from which full-depth coring (225 mm) was carried out, displays extensive map cracking (Fig. 1). Despite the somewhat alarming surficial condition of the concrete, Allard et al. [2] reported compressive strength and E-modulus values averaging 47.5 MPa and 24.5 GPa (each measured on six 100 mm cores), respectively. Interestingly, cores extracted from a somewhat "protected" section of the pavement (i.e. under a bridge structure) and showing only slight visual cracking, provided compressive strengths and E-moduli ranging from 57.7–62.9 MPa and 33.6–35.8 GPa, respectively [2]. Immediately after extraction, the cores were superficially dried and then wrapped in several layers of plastic sheets (cling film); the specimens were then brought to the laboratory where they were kept in a temperature-controlled room (12 °C) until ready for further processing. The core selected for microanalysis was first cut into 10 mm-thick slabs with a concrete saw (with water). The slabs were then examined with a stereomicroscope to identify aggregate particles with "large" cracks filled with ASR products (e.g. Fig. 2a), and further cutting was carried out to produce a proper size specimen for indentation testing.

The specimen was finely polished based on the protocol described by Leemann and Lura [28], with an additional polishing step with diamond suspension with size of 0.25 μm to further reduce the roughness. As described in Table 1, the surface of the specimen was first subjected to three polishing steps using SiC sandpapers with minimum amount of water. The fine finishing was then carried out using oil-based diamond suspensions and diamond paste (Table 1). The surface of the specimen was then protected in air-tight plastic bags and subjected to indentation testing within 24 h after the completion of the polishing operations, as done by Leemann and Lura [28]. Fig. 2 illustrates the specimen used for testing.

2.2. AFM and SEM\EDS techniques

Atomic force microscopy (AFM) allows the topographical scanning of the surface of a sample with high resolution (i.e. fractions of a nanometer) [31]. The AFM consists in a cantilever with a sharp tip (probe) that is used to scan the specimen surface. The AFM tests were carried out on a companion sample cut from the same concrete core, and which was polished with the same exact protocol that was used for the specimen (as explained in Table 1) used for nano and microindentation testing.

The specimen subjected to indentation testing was further examined by scanning electron microscopy (SEM – JEOL JSM-840A) using secondary electron (SE) imaging and energy dispersive X-ray spectroscopy (EDS). Operating conditions were set at 15 kV. Prior to SEM observations, the concrete specimen was gently dried for 24 h at 50 °C, and then coated with a thin layer of Au-Pd.

2.3. Basics of nanoindentation and microindentation

An indentation test consists of establishing contact between an indenter (typically diamond) and a sample, and subsequently measuring the load, P, and the penetration depth, h [13]. Fig. 3 shows a typical P–h curve for an indentation test with an initial constantly increasing load, followed by a short hold and then a unloading. By analyzing the P–h curve with a continuum model [16,19,40], the indentation hardness (H) and indentation modulus (M) can be derived as defined below:

$$H = \frac{P_{\max}}{A_C} \tag{1}$$

$$M = \beta \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A_C}} \tag{2}$$

where the coefficient β accounts for slip contact for a Berkovich shape tip; A_c is the projected area of the indenter at a distance h_c; $P_{\max}$ is the maximum load and $S = (dP/dh)_{h=h_{\max}}$ is the unloading indentation stiffness at the maximum penetration depth (h = $h_{\max}$). The latter can be estimated by the well-established Oliver and