Characterization of the Nano- and Microscale Deterioration Mechanism of the Alkali–Silica Reaction in Concrete Using Neutron and X-ray Scattering Techniques: A Review

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Abstract Alkali–silica reaction (ASR) is one of the most recognized chemical reactions that lead to the deterioration and premature failure of concrete. The severity of ASR is largely dependent on the expansive nature of the reaction product (ASR gel). As such, it is important to expound the developed knowledge on the formation, structure, composition, and swelling mechanism of ASR gel, to provide a greater understanding of ASR deterioration and to facilitate the development of more reliable prediction and mitigation methods. We present a summary of existing methods for assessing ASR and the state-of-the-art techniques that use neutron and X-ray scattering methods to characterize the nano- and microstructural properties of concrete and elucidate the potential transport dynamics of reactants that determine the mechanism and extent of ASR.

Keywords Alkali–silica reaction · Characterization · Microstructure · Nanostructure

1 Introduction

The alkali–silica reaction (ASR) is a deleterious chemical reaction that occurs in concrete when certain reactive silica phases in aggregates react with alkali ions (Na, K) from the pore solution [1–3]. Through decades of research the mechanism of ASR is relatively well documented, but controversy remains regarding the reported reaction sequence leading to the formation of ASR gel [4, 5] and the expansion

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mechanism of the gel to form cracks in concrete [6]. Undoubtedly, ASR begins with the dissolution of reactive silica in the alkaline pore solution of concrete and the dissolution rate depends on several factors including the degree of alkalinity of the pore solution, the type and particle size of the silica mineral present, temperature, and the presence of other cations such as Li^+, Al^{3+} and Ca^{2+} in the pore solution [1, 2]. Following silica dissolution, Ca^{2+} and alkali cations in the pore solution react with the dissolved silica to form a C-(Na, K)-S–H reaction product known as ASR gel, as well as other calcium-rich hydrates [2]. The composition and structure of the ASR gel may vary in the same concrete system, and in one concrete system from the other, depending on the location of the reaction site, the type and amount of silica and cations at the reaction site, and the age and curing conditions of the concrete. The contention in the sequence of ASR gel formation stems from an earlier proposal described by Hou et al. [4]. By comparing ASR gels in laboratory specimens to gels in field structures, those authors concluded that the continuous formation of a calcium-rich C-S-H product occurs when calcium is locally available at the reaction site [4]. This initial C-S-H is typically dense and acts as a physical barrier that isolates the reaction sites in the concrete structure [7]. Upon depletion of calcium at the localized sites, the concentration of silicon increases until a low calcium and high alkali C-(Na,K)-S-H ASR gel is formed at silicon saturation. Although this sequence of ASR gel formation has been supported by other studies [4, 8, 9], it is worth noting that the results were obtained from batch experiments using model reactant methods; thus, they may not be representative of actual concrete systems. Furthermore, a recently reported study [10] demonstrated that ASR gel may first form in cracks on the aggregate surface and around the aggregate, then penetrate towards the inside of the aggregate, which suggests that a C-S-H physical barrier may not be evident in the sequence of ASR gel formation. Moreover, once the ASR gel is formed, the mechanism by which it expands upon moisture absorption is still a topic of discussion [6, 11]. It is, however, well recognized that the addition of supplementary cementitious materials (SCMs) such as fly ash and slag effectively mitigates ASR in concrete [1, 12–14]. With the current depletion of these conventional SCMs, several studies are emerging to discover and optimize potential alternative SCMs and techniques for mitigating ASR. Understanding the dynamics of ASR gel formation, the transport of the gel through the concrete structure, the expansion mechanism of the gel and the effects of its expansion at the micro-and nanoscale is ultimately the key to developing effective mitigation against deleterious ASR. Currently, a number of techniques exist for assessing the structure and composition of ASR gel. In this paper we recap some of the reported studies on ASR characterization methods and present the state-of-the-art techniques that use neutron and X-ray scattering to identify the micro- and nanostructure of concrete to characterize additional features and propagation of ASR in concrete.

2 Traditional Characterization Techniques for Assessing ASR in Cement-Based Materials

Microscopic techniques such as petrography and scanning electron microscopy (SEM) are by far the most commonly used to identify ASR gel in concrete and other cement-based materials [15–18]. These methods can be used in conjunction with other techniques such as electron dispersive spectroscopy (EDS) [17], electron backscattered diffraction [19], Raman spectroscopy [20], nuclear microwave resonance (NMR) [21] and nonlinear impact resonance acoustic spectroscopy [22] to identify the morphology, composition and effect of ASR and its reaction products on concrete. A typical example of petrographic characterization of an ASR-affected mortar and concrete is presented in Fig. 1. Other less commonly used techniques that have shown proficiency in providing information on the nanostructure of cement-based materials and ASR are scanning transmission electron microscopy (STEM) [23, 24], atomic force microscopy [25] and scanning confocal microscopy [26].

Studies carried out by Leeman et al. [10, 27] to characterize the structure and composition of ASR gel formed in concrete using a combination of SEM–EDS, Raman spectroscopy and ^{29}Si NMR demonstrated that both crystalline and amorphous ASR products form in concrete aggregates. To follow the sequence of ASR gel formation and structure of the ASR products at the nanoscale, the studied concrete mixes were doped with $CsNO_3$ and KNO_3 tracers [10]. The authors established that ASR gel first forms in pre-existing pores or cracks in aggregates close to the cement paste and is generally amorphous in structure. The initial cracks that result from the expansion of the formed gel are mostly empty; therefore, secondary ASR products, identified as crystalline ASR gel, begin to fill the cracks while progressing from the aggregate–cement interface to the aggregate's interior. Further characterization in that study revealed that both the amorphous and crystalline ASR products have a structure dominated by Q^3-sites; however, there is a difference in their composition
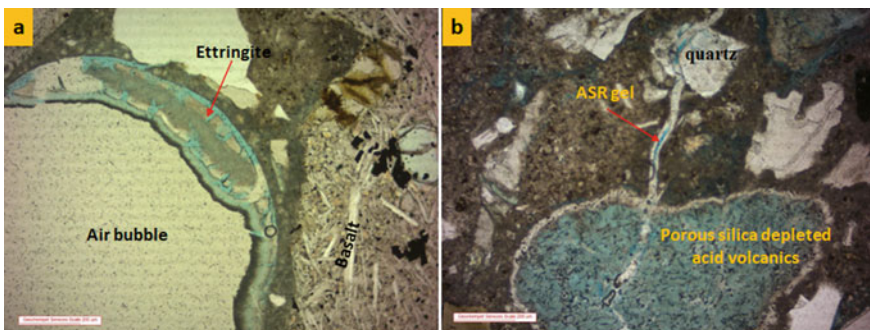

Fig. 1 Petrographic images of **a** concrete specimen showing ASR gel lining an air bubble that is thinly outlined by low birefringent ettringite and **b** ASR-filled crack passing through an acid volcanic fragment and a silica-depleted (porous) acid volcanic fragment

such that the amorphous product has a higher Na/K ratio. Additionally, ASR products in concrete samples cured at 38 °C exhibited a similar structure to ASR gel in field concretes, whereas at temperatures above 50 °C, a K-shylkovite structure was observed [27]. A similar observation has been reported in other studies [28, 29]. The difference in the ASR gel structure with temperature potentially contributes to the expansion capacity of the gel. This outcome supports that temperature is a significant factor to consider when selecting a suitable accelerated test method for assessing ASR, such as the accelerated concrete prism test and accelerated mortar bar test, and rationalizes the differences observed in the laboratory and field reactivity predictions of some aggregates.

Although these characterization methods are effective in assessing the microstructure and composition of ASR and other cement reaction products, they are generally destructive methods that depend on proper representative sampling from bulk material and somewhat rigorous sample preparation, which may influence the outcome of the characterization studies. For example, there are reports in the literature that cite instances where the sectioning and polishing of suspected ASR-affected samples for SEM analysis may have resulted in dislodgement of the ASR gel from cracks [30, 31]. Similarly, to obtain TEM lamellae for nanostructural characterization, cement-based samples are usually milled down to a low micron thickness (<3 µm) to allow the penetration of electron beams [24]. This potentially affects the structure of the formed product. The destructive nature of these methods also inhibits time-lapse characterization and continuous or in-situ monitoring of ASR development and crack propagation in the same region of the bulk sample. This is a major drawback to improving insight on the transport of reactants in concrete and identifying features of ASR that can contribute to the development of novel mitigation strategies.

3 X-ray and Neutron Scattering Techniques

Cement-based materials are characteristically porous. Pores play a key role in the durability and mechanical performance of concrete. For one, they act as a conduit, thus determining the extent of permeation of chemical agents and triggers of deterioration mechanisms. For example, during ASR, moisture containing alkali and other solutes may ingress from the service environment of the concrete structure or be transported from one region to the other within the concrete system through pores. Furthermore, as ASR gel takes up water and expands to form cracks, the propagation of the cracks provides a channel for the spread of less rigid, high-expansive ASR gel [32] through the concrete, promoting ASR. These cracks also become potential sites for the repolymerization and crystallization of new ASR products. However, it is worth noting that pores may be closed (air bubble) or open with a network of micro- and nanosized distribution. These features of the pore system are critical in understanding the influence and extent of porosity on the durability and strength of a concrete structure. For instance, during salt attack, the crystallization pressure of salts in the concrete will vary with pore size. Similarly, the mechanism of drying

shrinkage in the concrete is dependent on pore size and relative humidity such that in larger pores with higher relative humidity, capillary pressure is the driving force for drying shrinkage [33, 34]. Considering that the nature of the pore system in concrete has a major influence on its durability properties, destructive characterization techniques that generally sample thin sections from bulk concrete material may not provide precise information on pore features, including size, volume fraction, distribution, and network.

In the past decade, there has been a significant increase in the use of nondestructive neutron and X-ray scattering techniques, such as ultra-/small-angle neutron scattering (USANS, SANS), small angle X-ray scattering, X-ray computed tomography (X-ray CT) and neutron tomography, to characterize the micro- and nanostructure of the concrete and particularly to elucidate the chemo-poromechanics of ASR reactants through time-lapse damage evolution monitoring [35–37]. USANS and SANS use the elastic scattering of neutrons passing through a sample (neutron diffraction) to study the atomic structure of the bulk material and determine structural inhomogeneity at the mesoscopic scale length, typically ranging from 1 to 300 nm [38]. This technique is similar to X-ray diffraction as both principles obey the Beer Lambert law [39]. However, neutrons are unaffected by electrons, therefore when encountering matter, they penetrate to interact with the atomic nuclei whereas X-rays intermingle with the electron cloud around the atom [40]. As such, neutrons are relatively more sensitive to atoms with low atomic number such as hydrogen. This explicates the proficient use of neutron scattering techniques to characterize ASR gel (C-S-(Na,K)-H) and other cement hydrated reaction products, as well as the transport of reactant through the pores in the pore solution of concrete structures.

In tomography, neutron and X-ray beams passing through a sample are attenuated according to the sample's composition and geometry. A series of transmission images (tomographs) representing slices of the sample at several rotation angles are generated. These tomographs can be superimposed to form a 3D representation of the bulk sample showing the surface and internal features in respective volumetric locations [35, 41]. Typically, incident neutrons will provide a high imaging contrast for hydrates in concrete and a good transmittance of metals (e.g., steel reinforcements), whereas X-rays display a high contrast for metals and an adequate transmittance for other light element materials. Therefore, the information obtained from both scattering techniques is complementary. In characterizing concrete structures, the combined use of neutron and X-ray diffraction for imaging has proven to be very efficient for investigating the pore system, propagation of cracks, the presence and dynamics of reaction products, and monitoring of concrete reinforcement materials. For example, the neutron imaging facility at the Paul Scherrer Institute in Switzerland (NEUTRA) has in the past 7 years shown a development in imaging techniques by mounting an X-ray tube before the initial collimator to enable characterization of samples with X-rays and neutrons under the same geometric conditions and the use of an identical detection system [42]. A typical application of this bimodal approach to investigate the internal structure of stainless steel fiber-reinforced concrete is presented in Fig. 2.
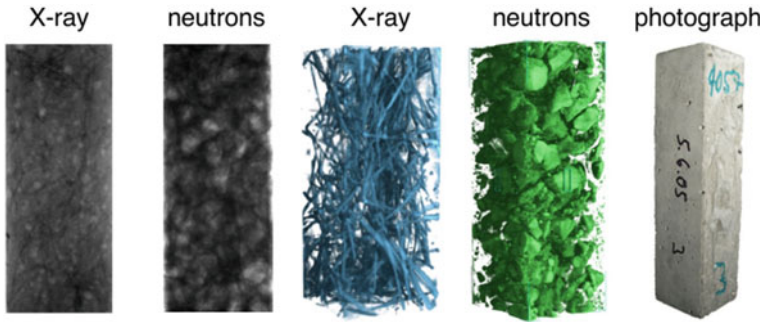
Fig. 2 Neutron and X-ray tomography of a concrete sample [42]

In Fig. 2, it can be seen that the neutron tomographic data set provides information on the segregation of aggregates and pore network in the concrete, whereas the X-ray tomographic results show detailed information on the steel reinforcement. In another study, the authors reconstructed a 3D microstructure of concrete using finite modelling by stacking 2D slices of the segmented concrete's microstructure obtained from both neutron and X-ray CT [41]. The reconstructed 3D microstructure, shown in Fig. 3, revealed the distribution and volume fraction of pores, aggregate and paste binder, as well as the sizes of the respective constituents.

Recently, the inclusion of nanomaterials in construction such the addition of carbon nanotubes as reinforcement in concrete to increase fire resistance, reduce porosity and improve strength properties, and the addition of novel nano- and micro-sized SCMs to improve strength and reduce ASR in concrete have become the focus of emerging research [43, 44]. The application of nondestructive neutron and X-ray techniques to understand how these new materials alter the microstructure of concrete to deliver the desired properties and performance is undoubtedly crucial in accomplishing such ground-breaking innovations.
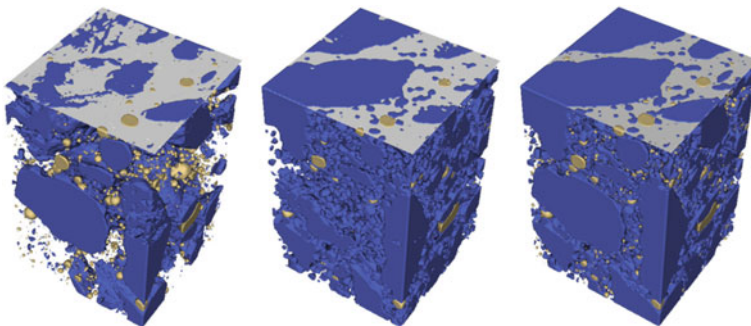

Fig. 3 Segmented aggregate and void phases obtained from **a** X-ray computed tomography (CT), **b** neutron CT, and **c** combined CT [41]

4 Conclusions

The characterization of ASR in concrete using microscopic and spectroscopic techniques have to date provided useful information that has contributed to the understanding of the mechanism of ASR and the development of mitigation measures. However, due to the destructive nature of these conventional techniques, crucial microstructural features that influence the dynamics, progression, and extent of ASR with age under different conditions are unobserved. To obtain these characteristics, non-destructive X-ray and neutron scattering techniques have shown excellent results, providing 3D volumetric insights into the morphology, interfacial bonding and interaction between constituents, and the pore system, which has a key effect on the durability of concrete. Nonetheless, X-ray and neutron scattering techniques usually do not provide information on the composition of the material. With advancements in the engineered materials used in construction, the ultimate characterization tool kit that combines microscopy and spectroscopy with neutron and X-ray scattering techniques will provide the best approach to understanding and optimizing the performance of concrete for modern structures.

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