Journal of Advanced Concrete Technology

Materials, Structures and Environment

Effect of alkalis on cementitious materials: Understanding the relationship between composition, structure, and volume change mechanism

Hailong Ye, Aleksandra Radlińska

Journal of Advanced Concrete Technology, volume 15 (2017), pp. 165-177

Related Papers Click to Download full PDF!

Performance of Different Grades of Palm Oil Ash with Round Steel Slag as Vascular Materials in the Synthesis of Alkaline Activated Mortar

Moruf Ajakaiye, Megat Azmi Megat Johari, Zainal Arifin Ahmed, Mohammed Maslehuddi

Journal of Advanced Concrete Technology, volume 12 (2014), pp. 378-387

Evaluation of alkalinity of pore solution based on the phase composition of cement hydrates with supplementary cementitious materials and its relation to suppressing ASR expansion

Yuichiro Kawabata, Kazuo Yamada

Journal of Advanced Concrete Technology, volume 13 (2015), pp. 538-553

Quantitative analysis of phase assemblage and chemical shrinkage of alkali-activated slag

Hailong Ye, Aleksandra Radlińska

Journal of Advanced Concrete Technology, volume 14 (2016), pp. 245-260

Click to Submit your Papers

Japan Concrete Institute <http://www.j-act.org>

Scientific paper

Effect of Alkalis on Cementitious Materials: Understanding the Relationship between Composition, Structure, and Volume Change Mechanism

Hailong Ye^{1*} and Aleksandra Radlińska²

Received 2 December 2016, accepted 29 March 2017

doi:10.3151/jact.15.165

Abstract

Previous studies demonstrated that alkalis can considerably affect the volumetric properties of hardened cementitious binders, including shrinkage, creep, and micro-cracking. The objective of this paper is to reexamine the effect of alkalis on the composition, nanostructure, phase stability, and morphology of calcium-silicate-hydrate (C-S-H) in cementitious materials, and to further propose a conceptual model bridging the C-S-H characters with its volume change mechanisms in alkali-enriched systems. The proposed microstructural model is an extension of the colloidal model of C-S-H considering the effect of alkalis. It is suggested that the presence of alkalis makes C-S-H more thermodynamically unstable and structurally disrupted, and easier to reorganize and redistribute upon drying-induced internal stresses or external loading. In addition, new experimental results regarding the influence of lithium on shrinkage and micro-cracking of alkali-activated blast-furnace slag are discussed. It shows that lithium addition can dramatically improve the cracking resistance and volumetric stability of alkali-activated slag.

1. Introduction

The alkali cation (mainly Na^+ and/or K^+) incorporated into hardened cement pastes and concrete can from either the composition of clinker (e.g., alkali sulfates) (Jawed and Skalny 1977), supplementary cementitious materials (SCMs) (Duchesne and Berube 1994), and aggregates (Rajabipour *et al.* 2015), or exposed alkali-bearing environments (e.g. deicing salts or seawater), or mixing solution (e.g. activator for alkali-activated calcium aluminosilicates (Thomas *et al.* 2016; Ye and Radlińska 2016b) or cement-SCMs blends (Lodeiro *et al.* 2009)). For cementitious binders, the incorporation of alkalis, either released from the dissolving solid reagents or directly added by mixing solution, can have dramatic impacts on its hydration kinetics, hydrated phase assemblage, composition and nanostructure of main hydrated phase, i.e., calcium-silicate-hydrate (C-S-H)¹, pore solution chemistry, and early-age properties (Jawed and Skalny 1978). For instance, regarding the volumetric properties of ordinary portland cement (OPC) paste, the alkali incorporation can increase autogenous and drying shrinkage magnitudes but reduce shrinkage kinetics (Juenger and Jennings 2001; Sant *et al.* 2012), and enhance micro-cracks formation. For alkali-activated calcium aluminosilicates (e.g. blast-

furnace slag), they inherently exhibit poor volumetric stability, showing up to six times higher shrinkage (Cartwright *et al.* 2014; Ye *et al.* 2014), extensive micro-cracks (Collins and Sanjayan 2001), and even disintegration (Guerrieri and Sanjayan 2011), in comparison to conventional OPC. Recent studies attributed this unique shrinkage characteristic (i.e. increased shrinkage magnitude but reduced shrinkage kinetics) of alkali-activated slag (AAS) to the alkali incorporation in the main hydrated product, i.e. calcium-alumina-silicate-hydrate (C-A-S-H) (Ye and Radlińska 2016c; Ye *et al.* 2017a).

However, from a microstructural perspective, the mechanisms of how the alkali cation can significantly affect the volume change mechanism of cementitious materials are still unclarified. Although extensive studies have been conducted in the literature regarding the effect of alkalis on the microstructure of cementitious materials, few studies have ever linked these alkali-induced microstructural changes to the volume change mechanisms of cementitious systems with alkali enrichment. As such, the paper first reviews the effect of alkalis on the nanostructure, composition, phase stability, and morphology of C-S-H, as it plays an overriding role in affecting the volumetric properties of cementitious materials.

Secondly, this paper summarizes the main findings of the effect of alkalis on the drying shrinkage, creep, and micro-cracking tendency of cementitious materials (mainly OPC and AAS). New experimental data regarding the effect of composition (e.g., Na/Si ratio) on the drying shrinkage of synthetic C-S-H and C-A-S-H is

¹Postdoctoral Research Associate, Department of Civil and Environmental Engineering, The Pennsylvania State University, State College, PA, 16801, USA.

*Corresponding author, E-mail: huy131@psu.edu

²Assistant Professor, Department of Civil and Environmental Engineering, The Pennsylvania State University, State College, PA, 16801, USA.

¹In Cement Chemistry notation: C = CaO, S = SiO₂, A = Al₂O₃, K = K₂O, N = Na₂O, H = H₂O

Table 1 Comparison of parameters in plain and NaOH-added hydrated OPC or C₃S.

Parameters	Plain OPC	OPC mixed with NaOH	Mixture (water-to-cement ratio, solution)	Reference
Nitrogen surface area (m ² /g D-dried paste)	35.0	18.7	w/c=0.45, 1M NaOH	(Juenger and Jennings 2001)
MIP porosity (%)	17.5	21.9	w/c=0.35, 0.5M NaOH	(Sant <i>et al.</i> 2012)
Ca/Si ratio of C-S-H	1.70	1.4-1.5	w/c= 0.35, 0.45M NaOH	(Mota Gassó 2015)
Mean chain length of C-S-H	4.5	3.0	w/c=0.6, 10% Na ₂ O by mass	(Mendoza <i>et al.</i> 2015)
	3.6	3.1	w/c=0.5, the same as above	

provided. More importantly, a new microstructure model of C-S-H, which conceptually links the alkali-induced compositional and microstructural changes to the macroscopic volumetric properties of cementitious materials, is proposed in this study. This model is an extended colloidal model of C-S-H which takes account of the effect of alkalis on composition, nanostructure, and colloidal nature of C-S-H.

On the other hand, this paper reports some new experimental findings regarding the influence of lithium hydroxide on the volumetric stability of AAS. Although the practical implementation of lithium compounds on AAS in the field is unlikely, this preliminary study aims to mainly demonstrate the effects of alkali types on its volumetric properties. These new results could shed some lights on understanding the effect of alkalis on alkali-activated materials, as well as the mechanisms of lithium compounds on improving the volumetric stability of concrete related to alkali-silica reaction (ASR).

2. Effect of alkalis on C-S-H

2.1 Nanostructure and composition

As supplied to the cementitious systems during hydration and/or hardening, the alkali can either remain in the pore solution or be bound by the hydrates. The amount of alkali ion uptake by the solid phases is dependent on the alkali concentration in the pore solution, pore solution chemistry (e.g. pH and the presence of other ions), and binding capacity of hydrates (Hong and Glasser 1999; Chen and Brouwers 2010). Several predictive models, such as the alkali partition theory (Taylor 1987), were proposed, establishing the correlation of alkali concentration in pore solution and alkalis content retained in solid phases. However, the binding mechanism of alkali cation in the hydrated phases, mainly C-S-H, is still inconspicuous in these models.

The mechanism of alkali binding in C-S-H can at least originate from two sources, i.e., surface adsorption and structural incorporation. The surface adsorption of alkalis on C-S-H is mainly to compensate the negative charge of silicate chains due to deprotonation of $\equiv\text{SiOH}$ to $\equiv\text{SiO}^-$ sites in the pore solution (Lothenbach and Nonat 2015). Therefore, the amount of alkalis bound to the surface is affected by the extent of deprotonation (e.g. pH-dependent), as well as the availability of other competing adsorbing cations (e.g. Ca^{2+}). For instance, the amount of uptake alkalis tends to increase with a decrease of Ca concentration and an increase of pH in pore solution (Lothenbach and Nonat 2015).

Nevertheless, the amount of uptake alkalis in C-S-H is not straightly proportional to the surface area of C-S-H, but highly affected by its chemical composition (e.g. Ca/Si ratio, incorporation of Al) (Myers *et al.* 2014; Provis *et al.* 2015). The nanostructure of C-S-H is somehow composition-dependent, which could, in turn, influence the structural binding of alkalis in C-S-H. First, ^{29}Si nuclear magnetic resonance (NMR) results show that the presence of alkalis can reduce the chain length of C-S-H (Mendoza *et al.* 2015) (see **Table 1**). Alkali can serve as a terminated cation at the end of the silicate chain and connects to non-bridging oxygen. Due to the structural incorporation of alkali in silicate chain, more calcium can be released to form the main calcium oxide layer at a constant total Ca/Si ratio (the total Ca/Si includes both main layer calcium and charge balancing calcium) (Lothenbach and Nonat 2015). The Ca/Si ratio of C-S-H tends to decrease due to the incorporation of alkalis (see **Table 1**). At high Ca/Si ratio, the effect of alkalis on the shortening of silicate chain is not significant, because the uptake of alkalis is prohibited by Ca, as the bivalent cations such as Ca^{2+} are preferred compared to monovalent Na^+ or K^+ due to a stronger electrostatic interaction. However, the results may change depending on alkali concentration, C-S-H composition, and the presence of other ions or solids. Besides incorporating into the silicate chain, alkalis may also enter the interlayer of C-S-H, as will be discussed later.

It should be emphasized that differentiating these two sites (or mechanisms) of alkalis binding in C-S-H nanostructure is challenging, since defining the nanostructure and surface characteristics of C-S-H itself are still controversial. According to the ^{23}Na NMR results, there are two different environments for Na in C-S-H, with two different capabilities of mobility (i.e. mobile Na and bound Na) (Viallis *et al.* 1999). The ^{23}Na NMR results also show that the fraction of bound Na decreases strongly with increasing Ca/Si ratio at low sodium concentration (total Na/Si = 0.1), and decreases much less at higher Na concentration (NaCl = 0.5 M). It indicates that these so-called bound Na and mobile Na are strongly correlated and interchangeable, which may correspond to the dynamic exchange between alkalis in these two sites (i.e. surface adsorption and structural incorporation). Furthermore, regardless of alkali binding mechanism, there may have a dynamic interaction between alkali and calcium cations, associating with the ion-exchange process.

Many studies also showed that there is no significant

difference between the amount of Na and K uptake in C-S-H (Stade 1989; Hong and Glasser 1999; L'Hôpital *et al.* 2016). However, some studies suggested that the binding capabilities are different for different types of alkali cations (e.g. Na^+ , K^+), implying an ionic size-dependence binding mechanism for alkalis in C-S-H (Bach *et al.* 2013). For example, X-ray diffraction shows that potassium does not change the *d*-spacing of the interlayer of C-S-H, while sodium reduces it. It was proposed that K, unlike Na, may enter the interlayer of C-S-H, in addition to the external surfaces, to compensate the negative charges in the interlayer (Bach *et al.* 2013). Nevertheless, contradictory findings were reported, showing that both Na and K can decrease the interlayer distance of C-S-H at high concentrations (L'Hôpital *et al.* 2016). The discrepancies among various studies might be a result of (1) comparing realistic C-S-H formed in the hydrated paste and synthetic C-S-H; (2) different synthesis methods and composition of C-S-H; (3) different types of cement; (4) different alkali concentrations.

2.2 Stability of C-S-H

The incorporation of alkalis into C-S-H tends to make the system less structurally and thermodynamically stable. By analyzing the influence of Na on synthetic C-S-H, it was found that the alkali addition, although hastens the formation of C-S-H, hinders the crystallization and precludes the transformation of this intermediate product into a higher order crystalline structure (NocuŃ-Wczelik 1999). In addition, XRD pattern of hydrated alites blended with alkali hydroxide solution shows a broadening at the base of the peaks, at around 29.0° (2 θ) (Mendoza *et al.* 2015), which may be associated to a decreased crystallinity of C-S-H. If alkali cation is incorporated into the interlayer of C-S-H, it may induce additional structural disorder, both by reducing the periodicity of the interlayer and by reducing the regularity of the stacking of the layers through differences in ionic size (Provis *et al.* 2015).

As alkalis modify the nanostructure and composition of C-S-H, it may favor the formation of a Ca-containing alkali-silicate-hydrate (N-S-H) phase when alkali is extensively bound (Lodeiro *et al.* 2009). The Ca-containing N-S-H or N-A-S-H is typically identified in the hydration products of alkali-activated low-calcium aluminosilicates (e.g. Class F fly ash-based geopolymer) (Provis and Van Deventer 2009; Ye and Radlińska 2016a). However, the long-term stability of alkali incorporation into the structure of C-S-H, C-A-S-H, or N(-A)-S-H, is still unclear. Early Russian literature suggests that alkali ions play a catalytic role in the early stages of hydration, involving an ionic exchange with Ca^{2+} cations (Shi *et al.* 2006). While in the late stages of hydration, alkali cations can serve as a structure-forming component in alkali-containing hydrated phases. As the amount of alkali bound to C(-A)-S-H is significant, regardless of the binding mechanisms (catalytic or

structural forming effect), a metastable form of N-C(-A)-S-H may form. This N-C(-A)-S-H can be treated as a solid solution between C(-A)-S-H and N(-A)-S-H. The direct mixing of pre-synthesized C-S-H or C-A-S-H with N-A-S-H leads to a gradual degradation of N-A-S-H to C-A-S-H (Garcia-Lodeiro *et al.* 2011). In other words, N-A-S-H can be de-stabilized by Ca to give C(-N)-A-S-H, and its stability is dependent on the availability of Ca and pH in the solution. This observation is not surprising as Ca^{2+} can override alkali cation on adsorbing on or incorporating into the silicate structure due to a stronger electrostatic attraction force.

In conventional pure OPC system, most alkali ions are contained in the pore solution in mature cement pastes, and the typical ratios of structurally contained alkali to Ca in C-S-H of OPC pastes are under 0.01 for Na (Taylor 1997). This could be attributed to the instability of alkali incorporation in C-S-H especially as it has a high Ca/Si ratio. This small amount of alkali binding can readily be accommodated in the interlayer sites of C-S-H, without have a structural forming function.

In the hydrated phases of alkali-activated materials or alkali-silica gels formed in ASR, the initial amount of alkalis remaining in the phases are significant. However, the composition of the phase may undergo dramatic compositional and structural evolutions as hydration or reaction continues. For example, the (Na+K)/Si ratio and Ca/Si ratio of alkali-silica gels can respectively change from 0.3 to below 0.01, and 0.3 to 1.6, for concrete from 7 to 55 years old (Thomas 2001). The composition of ASR gels at long-term is very close to that of C-S-H, indicating a cation exchange with the Ca^{2+} replacing the alkali in the initially alkali-enriched products. Similarly, the Ca/Si and K/Ca ratios in the inner products of C-A-S-H observed in AAS can respectively increase from 1.15 to 1.18, and decrease from 0.13 to 0.09 as hydration continues from 1 to 8 years (Richardson *et al.* 1994).

2.3 Morphology of C-S-H

For plain C-S-H, the morphologies for inner and outer products are reported to be different. Inner products typically have a fine-scale and homogeneous morphology with pores somewhat under 10 nm in diameter, while the outer products present in a fibrillar morphology (Richardson 1999). The morphology of C-S-H transforms from a fiber or honeycomb-like to foil-like when alkalis are added (Macphee *et al.* 1989). More specifically, for plain OPC, the C-S-H needles grow in isolated clusters, while with alkalis, the needles are less well defined and do not grow much out from the surface. Prior to illuminating the modification mechanisms of C-S-H morphology due to alkali enrichment, one unsolved question is the difference in C-S-H nature between fiber-like and foil-like morphologies. According to Jennings and his coworkers (Thomas *et al.* 1998), the two different morphologies of C-S-H may be correlated to the different packing densities of C-S-H clusters. The

experimental results shown in **Table 1** indicate that the alkalis addition can reduce the surface area of OPC, which may be related to the changes in the packing density and morphology of C-S-H.

In addition, for hydrated slag, including slag blended cement, water-activated slag, and alkali-activated slag, the foil-like morphology becomes more prevalent. This modification may also be attributed to the changes in composition and nanostructure of C-S-H. Since for low Ca/Si ratio and high pH solution, which are typically the case for hydrated slag system, it tends to increase the uptake of alkalis as mentioned before.

2.4 Interaction of alkalis with alumina

Alumina can bind into the structure of C-S-H, either substituting the Si in bridging sites (tetra-coordinated) in the silicate chains, or partially substituting Ca on the C-S-H interlayer or surface (penta-coordinated and/or hexa-coordinated) (Faucon *et al.* 1999). The substitution of silicon by aluminum in the bridging tetrahedron is calculated to show the strongest stabilization of the C-S-H structure by *ab-initio* calculations (Abdolhosseini Qomi *et al.* 2012). However, the proportion and type of alumina binding sites may vary depending on the C-S-H composition and surrounding aqueous chemistry.

Alumina can be described as a network forming agent, which can either increase the length chain (i.e. polymerization of (alumina-) silicate) or create bridging between adjacent C-S-H layers. However, as Al^{3+} is connected to two bridging oxygen, the charge deficit typically needs to be balanced by alkalis or Ca^{2+} in the near vicinity of the aluminum site. The amount of aluminum incorporated into the C-S-H phase is partly controlled by the available quantity of alkali ions. More specifically, previous experiments show that the alkali ions promote the incorporation of Al in the bridging sites of the silicate chains of C-S-H (Skibsted and Andersen 2013). In return, the addition of Al can increase the alkali binding capability of C-S-H (Hong and Glasser 2002).

3. Influence of alkalis on volumetric stability

3.1 Drying Shrinkage

A straightforward approach for investigating the effect of alkalis on the drying shrinkage of C-A-S-H in cementitious materials would be studying the shrinkage of synthetic C-A-S-H. **Figure 1** shows the time-dependent shrinkage and mass changes, and correlation of shrinkage and mass changes for synthetic C-A-S-H dried at 50% relative humidity (RH) (purged with dry nitrogen gas to minimize carbonation). The C-A-S-H with various compositions were synthesized by mixing oven-dried colloidal SiO_2 powder, reagent grade $Ca(OH)_2$ powder, $Al(OH)_3$ powder, and NaOH solution or distilled water. The mix proportion of synthetic C-A-S-H is listed in **Table 2**. Other details of the experiments are

provided in the captions of **Fig. 1**. Based on this preliminary study, it can be seen that when the Na/Si is high than 0.2, the drying shrinkage of C-A-S-H is sig-

Fig. 1 (a) Time-dependent length change; (b) Time-dependent weight change; (c) Correlation between length change and weight change for synthetic N-C-A-S-H with various Na/Si and Al/Si ratios but constant Ca/Si ratio and water content, dried at 50% RH, 23 ± 0.5 °C (nitrogen purged). The mix proportion is listed in Table 2. The measurements were terminated when the specimens were disintegrated.

Table 2 Mix proportion of synthetic (N-)C-A-S-H paste.

Mixture Parameters	Mixture ID						
	M1	M2	M3	M4	M5	M6	M7
Ca/Si (mole ratio)	1	1	1	1	1	1	1
Na/Si (mole ratio)	0.4	0.4	0.4	0.4	0	0.2	0.6
Al/Si (mole ratio)	0	0.05	0.1	0.2	0.1	0.1	0.1
H ₂ O to solid ratio (wt./wt.)	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Total mass (g)	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
Ca(OH) ₂ (g)	288.16	282.55	277.15	266.96	305.53	290.65	264.85
NaOH (g)	58.88	57.73	56.63	54.55	0.00	27.97	82.75
Al(OH) ₃ (g)	0.00	14.89	29.21	56.28	32.20	30.64	27.92
Colloidal SiO ₂ (g)	236.30	231.70	227.27	218.91	250.55	238.34	217.19
H ₂ O (g)	416.66	413.13	409.73	403.31	415.35	412.40	407.29
Solution molarity (M)	3.53	3.49	3.46	3.38	0.00	1.70	5.08

nificantly increased. The amount of Al does not significantly affect the shrinkage magnitude of C-A-S-H at a constant Na/Si ratio. However, it seems that the Al addition can enhance its cracking resistance, as the one with a higher Al/Si ratio shows a higher volumetric integrity during drying. The XRD analysis (see **Fig. 2**) of synthetic C-A-S-H shows that the Al(OH)₃ powder was not completely dissolved and the amount and/or crystallinity of C-A-S-H were different among various mixtures.

The study of OPC mixed with high alkalinity solutions (i.e., 2M NaOH, 2M NaCl, and 2M KOH) does show that the effect of alkalis on shrinkage is significant (Ye *et al.* 2017b). The addition of alkalis dramatically increases the drying shrinkage magnitude but reduces the shrinkage kinetics of OPC, regardless its source (Blaine 1968; Beltzung *et al.* 2008; Ye *et al.* 2017b). Moreover, the shrinkage of AAS shows up to 6 times higher than that of OPC in magnitude and exhibits a visco-elastic/visco-plastic characteristic. This unique shrinkage behavior observed in alkali-enriched OPC or

AAS can both be attributed to the high level of alkalis in the system.

The significant effect of alkalis on shrinkage performance of cementitious materials can be explained by the capillary pressure theory. According to capillary pressure theory, the formation of menisci in capillary pores can generate hydrostatic pressure, which pulls adjacent solid particle closer, resulting in shrinkage. The magnitude of capillary pressure in a capillary pore where a meniscus is stably formed can be correlated to the RH at equilibrium condition using Kelvin equation, as well as the radius of meniscus using Young-Laplace equation (Adamson and Gast 1967):

$$p_c = \frac{\rho_l RT}{M_l} \ln \left(\frac{RH}{RH_s} \right) = - \frac{2\gamma \cos \theta}{r_c - t} \quad (1)$$

In which the RH is the measured relative humidity [%]; RH_s is the contribution to the RH due to salts in the pore fluid, which can be approximated as the water

Fig. 2 XRD patterns of synthetic C-A-S-H paste after 28d moist curing. They were acquired in a conventional Bragg-Brentano θ - 2θ configuration. CuK α X-ray ($\lambda=1.5418 \text{ \AA}$) was generated using 40 mA and 45 kV operating conditions.

activity, x_w , for ideal solution [%]; ρ_l is the density of liquid [kg/m³], M_l is the molar mass of liquid [kg/mol], $R = 8.314$ [J/(mol·K)] is the universal gas constant, T is the temperature [K]; r_c is the capillary radius at the position of meniscus (i.e. Kelvin radius) [m], γ is the surface tension between pore water and vapor [N/m], θ is the contact angle denoting the hydrophilicity of the pore wall [°], and t is the thickness of an adsorbed layer [m], which is a function of RH (Wittmann 1973; Badmann *et al.* 1981).

According to Eq. (1), the Kelvin radius, which is the radius of the largest capillary pore filled with water at equilibrium condition, can be calculated. Therefore, under equilibrium condition, all surface pores whose radii are smaller than the Kelvin radius are completely filled with water, whereas larger surface pores are dried and only contain a layer of adsorbed water with a thickness of t . Since only the pores which are saturated with capillary water can contribute to the formation of capillary pressure, the *effective capillary pressure* can be approximated by multiplying the capillary pressures p_c with the degree of saturation S_w , i.e. $S_w p_c$ (Mackenzie 1950; Bentz *et al.* 1998; Bentz 2005). Therefore, the linear shrinkage strain resulting from the internal capillary pressure for isotropic elastic materials can be calculated using:

$$\varepsilon_{cap} = -\frac{S_w p_c}{3} \left(\frac{1}{K} - \frac{1}{K_s} \right) \quad (2)$$

In which ε_{cap} is the capillary pressure-driven linear shrinkage strain, K is the bulk modulus of the whole porous body [Pa], K_s is the bulk modulus of the solid material [Pa].

According to Eq. (2), for the elastic shrinkage, the high magnitude of shrinkage can be attributed to a high effective capillary pressure, degraded K , or increased K_s . According to mercury intrusion porosimetry data, the porosity of OPC can be enlarged due to alkaline enrichment, resulting in a reduced K (Sant *et al.* 2012). Based on nano-indentation tests, the elastic modulus of C-S-H aggregations can increase, probably resulting in an increased K_s (Mendoza *et al.* 2015). On the other hand, as the increased alkali concentration in pore solution typically reduces the water activity, the magnitude of capillary pressure would decrease based on Raoult's law (Lura *et al.* 2010). However, the reduced water activity increases the value of Kelvin radius, which conversely increases the S_w for the same pore structure. Considering that the pore structure of systems with alkalis can be coarser or finer depending on the type of alkalis, the value of effective capillary stress ($S_w p_c$) may not dramatically change in the alkali-enriched system.

In fact, the direct implementation of Eq. (2) significantly underestimates the magnitude of shrinkage measured for OPC and AAS, and cannot explain the delayed shrinkage kinetics observed for the system with alkali enrichments. The primary reason is that Eq. (2) is based

on the assumption that drying-induced deformation is elastic, which seems to be seriously violated for the case of cementitious materials with alkalis. The delayed shrinkage kinetics and visco-elastic/visco-plastic characteristic indicate that the alkalis promote the irreversible shrinkage component in cementitious materials. The detailed description of the effect of alkalis on the volume change mechanisms will be provided in the extended colloidal model of C-S-H in Section 4.

3.2 Creep

There is limited information in the literature regarding the effect of alkalis on the creep behaviors of OPC. However, for AAS, a previous study (Collins and Sanjayan 1999) shows that plain OPC shows larger creep than AAS during the first three days, but shows much smaller creep than AAS at the longer term. The creep deformation can be sub-divided into reversible (short-term) and irreversible (long-term) components. The reversible component is typically related to the micro-diffusion of water between capillary pores, while the irreversible component is attributed to the rearrangement and redistribution of C-S-H (Ye 2015). Therefore, the delayed accumulation of creep in AAS is likely to indicate that more proportion of creep deformation in AAS is irreversible. As a consequence, the alkalis can potentially promote the irreversible deformation under external loading, which is in strong agreement with the previous argument that alkalis promote irreversible deformation under drying. This is not likely to a coincident but implies that alkalis inherently affect the volumetric change behaviors of C-S-H.

3.3 Micro-cracking and self-healing

It has been documented that AAS exhibits extensive surface micro-cracking at drying condition (Collins and Sanjayan 2001). The origin of the extensive micro-cracking, although still unclear, could also be directly related to the alkalis. This argument is supported by the fact that OPC mixed with 2M NaOH exhibits extensive map cracking at the surface after drying for 4d, which is analogous to the cracking performance observed in AAS (see Table 3). The mechanisms of surface cracking could be attributed to the more heterogeneous microstructure and/or refined pore structure in alkali-enriched systems, which create higher internal stresses and/or differential stresses. However, it is interesting to notice that the initially-formed surface cracks in AAS and alkali-enriched OPC can self-heal after drying for about 30d. The mechanisms of self-healing could be attributed to the continued hydration and/or stress relaxation due to the microstructural reorganization of C-S-H.

4. A new model of C-S-H with alkalis

The model proposed here attempts to extend the colloidal model of C-S-H originally proposed by Jennings and his coworkers (Jennings 2000; Jennings 2008) by con-

Table 3 Comparison of the surface micro-cracking development in plain OPC, OPC mixed with 2M NaOH, and NaOH-activated slag after being exposed to 50% RH, 23±0.5 °C with nitrogen purged environmental chambers.

Mixture	Drying at 50% RH, 23±0.5 °C for 4d	Drying at 50% RH, 23±0.5 °C for 10d	Drying at 50% RH, 23±0.5 °C for 30d
OPC
OPC with 2M NaOH
4M NaOH-activated slag

sidering the effect of alkalis. The extended model concerns specifically the relationship between the alkali-induced microstructural changes in C-S-H and the volume change mechanisms of alkali-enriched systems, in term of irreversible shrinkage and creep.

According to the colloidal model proposed by Jennings (Jennings 2000; Jennings 2008), the C-S-H is described as an aggregation of precipitated colloid size particles. As illustrated in **Fig. 3**, the nanostructure of C-S-H is an assemblage of basic blocking particle ‘globule’, which is a disk-like object with a thickness of around 4 nm and a layered internal structure similar to tobermorite and jennite. The packing of these globules produces a multi-scale porous structure. Given the granular nature of C-S-H, the irreversible (permanent) deformation can be attributed to the rearrangement and redistribution of C-S-H nanoparticles, resulting in denser nanoparticles packing and reduced surface area.

In comparison with the original model, the model proposed in this study suggests that alkalis can reduce the staking regularity of C-S-H nanoparticles due to the alkalis incorporation at very early age of hydration. Under drying-induced internal stresses or external loading, the alkalis cation can play an important role during the

organization and redistribution processes of C-S-H clusters. As shown in **Fig. 4**, the partial replacement of Ca^{2+} by alkali cation introduces additional structural disorder in C-S-H interlayer due to differentiating ionic size. Moreover, the structural incorporation of alkali cation makes the silicate network more disconnected and distorted, showing a smaller size of C-S-H nanoparticles. As such, under the same amount of stresses, the alkali-enriched system can undergo much easier rearrangement and reconstruction, as the alkalis in C-S-H facilitates these processes. In particular, the mobile alkali cations adsorbed at the external surfaces of C-S-H clusters or remained at the interlayer of C-S-H could contribute to the sliding of C-S-H layers or clusters relative to each other. As a consequence, the alkali enrichment in C-S-H can result in a denser packing of C-S-H clusters, as illustrated in **Fig. 3**. Alternatively, this model suggests that the C-S-H layered structure becomes easier to collapse when alkalis are extensively bound, in comparison to the plain system.

This model explains the unique deformation characteristics of alkali-enriched cementitious systems. It indicates that the increased shrinkage magnitude, delayed shrinkage kinetics, and increased long-term creep de-

formation due to alkali enrichment, can all be attributed to the fact that alkali-enriched C-S-H is basically a visco-elastic/visco-plastic material with considerable low viscosity. In other words, the alkali enrichment in C-S-H increases its visco-elastic/visco-plastic compliances. The visco-elastic/visco-plastic nature of C-S-H can be linked to the reorganization and redistribution of C-S-H nanoparticles as mentioned before.

As microstructural arrangement progresses under dry-

ing or loading, a consequence of physical, chemical, and properties changes in C-S-H could occur. For example, the alkali cation would be expelled during the reorganization, probably due to its less thermodynamically favorability to silicate chain compared to Ca^{2+} , resulting in polymerization among broken silicate chains. The structure of C-S-H would become more ordered as alkali cation is progressively expelled and more polymerized with stronger networks. Simultane-

Fig. 3 Illustrations of C-S-H clusters (a) before drying/loading in plain C-S-H; (b) after drying/loading in plain C-S-H; (c) before drying/loading in alkali-enriched C-S-H; (d) after drying/loading in alkali-enriched C-S-H.

Fig. 4 Illustration of the effect of alkalis incorporated into C-S-H on the reorganization and redistribution process of C-S-H nanoparticles under internal or external stresses. It should be noted that the orientation of applied stresses is merely for demonstration and does not imply that the shearing stresses are the only driving forces for C-S-H redistribution. (For the middle figure, Green polyhedra = CaO , blue tetrahedra = SiO_2 , red spheres = inter layer O, green spheres = interlayer Ca, yellow spheres = Alkali cations).

ously, the composition and density of C-S-H would vary and increase as drying or loading proceeds. However, it should be noted that the nature and magnitude of stresses in C-S-H nanostructure would be different for the same system under drying and loading (Ye 2015).

Although hypothetical, this model suggests that the driving force for the easy rearrangement of C-S-H is the thermodynamical instability of alkali-enriched C-S-H. The model predicts that the addition of Al^{3+} or other network forming agents may improve the volumetric stability of alkali-enriched C-S-H. In addition, promoting the structural stability of C-S-H, through heat treatment or aging, would also enhance its volumetric stability.

5. Some notes on the effect of lithium

After recognizing the effect of sodium and/or potassium cations on the volumetric instability of cementitious

materials, it would be interesting to examine the effect of lithium as well, for at least two reasons. One is that lithium cation is also a member of alkali metals like sodium and potassium, but with a different atomic size and field strength. Secondly, lithium compounds have been used to enhance the volumetric stability associated with ASR in concrete.

As such, some preliminary data regarding the effect of lithium on the volumetric stability of AAS is, for the first time, reported here. Particularly, the drying shrinkage and surface cracking maps of AAS prepared by various combinations of NaOH and LiOH solutions were monitored. The details of the experiment can be found in the caption of Fig. 5. The main finding is that replacement of NaOH by LiOH slightly reduces the shrinkage magnitude, but the change is not significant. However, the surface cracking resistance and volumetric stability of AAS is dramatically improved by LiOH, especially when the (LiOH)/(NaOH) mole ratio is larger

Fig. 5 (a) Time-dependent shrinkage development; (b) Time-dependent weight change; (c) Correlation between shrinkage and weight change, for 4M (Na, Li)OH-activated slag, with mole ratios of (NaOH)/(LiOH) in the activator as 100/0, 75/25, 50/50, and 25/75. The solid lines represent the samples being dried at to 50% RH, $23 \pm 0.5^\circ\text{C}$ (nitrogen purged) for 100d after 1d moist curing (100% RH, $23 \pm 0.5^\circ\text{C}$), while the dash lines represent the samples being dried at to 50% RH, $23 \pm 0.5^\circ\text{C}$ (nitrogen purged) for 40d after curing at 90%RH, $23 \pm 0.5^\circ\text{C}$ for 60d. It should be noted that the measured shrinkage may include the cracking effect during the drying.

Table 4 Comparison of the surface cracking and volumetric stability of AAS prepared by various combined NaOH and LiOH solutions dried at two conditions purged with dry nitrogen gas. It can be seen that prior curing at 90% RH before drying at 50% RH exacerbates the micro-cracking and results in significant disintegration of NaOH-activated slag. That may be attributed to the decreased permeability in AAS caused by pore refinement during pre-conditioning at 90%RH.

Type of activator	Direct drying to 50% RH, 23±0.5 °C for 100d	Conditioned at 90% RH, 23±0.5 °C for 60d, then dried at 50% RH, 23±0.5 °C for 40d
100% LiOH
75% LiOH + 25% NaOH
50% LiOH + 50% NaOH
25% LiOH + 75% NaOH

than 1.0 (see **Table 4** for details). It is concluded that the addition of lithium into AAS can improve its resistance against shrinkage cracking.

Although the mechanisms of Li on improving the cracking resistance of AAS and on suppressing ASR reaction may not be identical, we could postulate the potential influence of Li on AAS based on the previous ASR studies. It should be noted that the exact suppressing mechanisms of lithium compounds (e.g., LiOH, Li₂CO₃, and LiNO₃) on ASR expansion in concrete remain controversial; however, it is generally believed that there is some interaction between lithium and alkali-silica gels. It has been proposed that the Ca/Si ratio of the alkali-silica gel decreases with the increasing addition of LiOH and Li₂CO₃ (Kawamura and Fuwa 2003; Mo 2005). This observation is not surprising as Na and K have the similar effects on the composition of C-S-H as discussed in Section 2.1. However, compared to Na and K, lithium seems to preferentially react with silica (Rajabipour *et al.* 2015) and could form a crystalline lithium-silicate compound and a Li-bearing, low-Ca silica gel (Feng *et al.* 2010). This behavior may be at-

tributed to the smaller ionic radius and higher charge density of lithium, in comparison to Na and K (Mo 2005). Therefore, it could be postulated in this study that the addition of Li in AAS systems can expel the Na and K out of the structure of C-S-H, thus enhancing its structural stability. This hypothesis is in agreement with the model proposed in Section 4 and implies that the Li-rich C-S-H phase can be stable even in the presence of Ca²⁺ in the pore solution. Nevertheless, further studies are needed to verify these research hypotheses.

Conclusions

The main contribution of this paper is to provide a thorough understanding of the effect of alkalis on the C-S-H and link these alkali-induced compositional and structural modifications to the observed macroscopic volumetric change mechanisms of cementitious binders. Following conclusions can be drawn based on this study:

- (1) Based on the literature survey, it is found that the incorporation of alkalis into C-S-H can lower Ca/Si

ratio, shorten silicate chain length, increase the extent of the structural disorder, make it more thermodynamically unstable, and exhibit foil-like morphology. In addition, alkalis addition generally increases the magnitude of deformation but reduces the deformation kinetics of C-S-H.

- (2) An extended colloidal model of C-S-H by taking account of the effect of alkalis is proposed in this study. Although the model is merely conceptual and qualitative, it explains the observed volume change of cementitious materials based on the reported microstructure changes in C-S-H.
- (3) The model suggests that alkali cation makes C-S-H easier to rearrange and reorganize under stresses or loading, which may be attributed to the thermodynamic instability of the alkali-enriched C-S-H system.
- (4) Alkalis promote early-age drying-induced microcracking in OPC and AAS; however, these microcracks can self-heal probably due to continued hydration and/or stress relaxation as a result of the microstructural reorganization.
- (5) Lithium does not significantly affect the shrinkage performance of NaOH-activated slag but can improve its cracking resistance and volumetric stability.

Acknowledgements

The authors gratefully acknowledge the financial support from the U.S. National Science Foundation (NSF) under Award CMMI #1265789. Any opinions, findings and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the NSF.

References

- Abdolhosseini Qomi, M. J., Ulm, F. J. and Pellenq, R. J. M., (2012). "Evidence on the dual nature of aluminum in the calcium-silicate-hydrates based on atomistic simulations." *Journal of the American Ceramic Society*, 95, 1128-1137.
- Adamson, A. W. and Gast, A. P., (1967). "Physical chemistry of surfaces." 6th ed. New York: Wiley-Interscience.
- Bach, T., Chabas, E., Pochard, I., Coumes, C. C. D., Haas, J., Frizon, F. and Nonat, A., (2013). "Retention of alkali ions by hydrated low-pH cements: Mechanism and Na⁺/K⁺ selectivity." *Cement and Concrete Research*, 51, 14-21.
- Badmann, R., Stockhausen, N. and Setzer, M. J., (1981). "The statistical thickness and the chemical potential of adsorbed water films." *Journal of Colloid and Interface Science*, 82, 534-542.
- Beltzung, F., Wittmann, F. and Wan, X., (2008). "Influence of alkali content on creep and shrinkage of cement-based materials." In: Sun, W., van Breugel, K., Miao, C., Ye, G. and Chen, H., Eds. *Proceedings of the International Conference on Microstructure Related Durability of Cementitious Composites*, RILEM Publications, 905-915.
- Bentz, D. P., (2005). "Curing with shrinkage-reducing admixtures." *Concrete International*, 27, 55-60.
- Bentz, D. P., Garboczi, E. J. and Quenard, D. A., (1998). "Modelling drying shrinkage in reconstructed porous materials: application to porous Vycor glass." *Modelling and Simulation in Materials Science and Engineering*, 6, 211-236.
- Blaine, R., (1968). "A statistical study of the effects of trace elements on the properties of Portland cement." In: *Proceedings of the Proc 5th Int'l Symp Chemistry of Cement*, Tokyo, 86-91.
- Cartwright, C., Rajabipour, F. and Radlińska, A., (2015). "Shrinkage characteristics of alkali-activated slag cements." *Journal of Materials in Civil Engineering*, 27, B4014007.
- Chen, W. and Brouwers, H., (2010). "Alkali binding in hydrated Portland cement paste." *Cement and Concrete Research*, 40, 716-722.
- Collins, F. and Sanjayan, J., (1999). "Workability and mechanical properties of alkali activated slag concrete." *Cement and Concrete Research*, 29, 455-458.
- Collins, F. and Sanjayan, J., (2001). "Microcracking and strength development of alkali activated slag concrete." *Cement and Concrete Composites*, 23, 345-352.
- Duchesne, J. and Berube, M.-A., (1994). "Available alkalis from supplementary cementing materials." *ACI Materials Journal*, 91, 289-299.
- Faucon, P., Delagrave, A., Petit, J., Richet, C., Marchand, J. and Zanni, H., (1999). "Aluminum incorporation in calcium silicate hydrates (CSH) depending on their Ca/Si ratio." *The Journal of Physical Chemistry B*, 103, 7796-7802.
- Feng, X., Thomas, M., Bremner, T., Folliard, K. J. and Fournier, B., (2010). "Summary of research on the effect of LiNO₃ on alkali-silica reaction in new concrete." *Cement and Concrete Research*, 40, 636-642.
- Garcia-Lodeiro, I., Palomo, A., Fernández-Jiménez, A. and Macphee, D., (2011). "Compatibility studies between NASH and CASH gels. Study in the ternary diagram Na₂O-CaO-Al₂O₃-SiO₂-H₂O." *Cement and Concrete Research*, 41, 923-931.
- Guerrieri, M. and Sanjayan, J., (2011). "Investigation of the cause of disintegration of alkali-activated slag at temperature exposure of 50°C." *Journal of Materials in Civil Engineering*, 23, 1589-1595.
- Hong, S.-Y. and Glasser, F., (1999). "Alkali binding in cement pastes: Part I. The CSH phase." *Cement and Concrete Research*, 29, 1893-1903.
- Hong, S.-Y. and Glasser, F., (2002). "Alkali sorption by CSH and CASH gels: Part II. Role of alumina." *Cement and Concrete Research*, 32, 1101-1111.
- Jawed, I. and Skalny, J., (1977). "Alkalies in cement: A review I. Forms of Alkalies and their effect on clinker

- formation." *Cement and Concrete Research*, 7, 719-729.
- Jawed, I. and Skalny, J., (1978). "Alkalies in cement: a review: II. Effects of alkalies on hydration and performance of Portland cement." *Cement and Concrete Research*, 8, 37-51.
- Jennings, H. M., (2000). "A model for the microstructure of calcium silicate hydrate in cement paste." *Cement and Concrete Research*, 30, 101-116.
- Jennings, H. M., (2008). "Refinements to colloid model of CSH in cement: CM-II." *Cement and Concrete Research*, 38, 275-289.
- Juenger, M. C. G. and Jennings, H. M., (2001). "Effects of high alkalinity on cement pastes." *ACI Materials Journal*, 98.
- Kawamura, M. and Fuwa, H., (2003). "Effects of lithium salts on ASR gel composition and expansion of mortars." *Cement and Concrete Research*, 33, 913-919.
- L'Hôpital, E., Lothenbach, B., Scrivener, K. and Kulik, D., (2016). "Alkali uptake in calcium alumina silicate hydrate (CASH)." *Cement and Concrete Research*, 85, 122-136.
- Lodeiro, I. G., Macphee, D., Palomo, A. and Fernández-Jiménez, A., (2009). "Effect of alkalis on fresh C-S-H gels. FTIR analysis." *Cement and Concrete Research*, 39, 147-153.
- Lothenbach, B. and Nonat, A., (2015). "Calcium silicate hydrates: Solid and liquid phase composition." *Cement and Concrete Research*, 78, 57-70.
- Lura, P., and Lothenbach, B., (2010). "Influence of pore solution chemistry on shrinkage of cement paste." In: Miao, C., Ye, G. and Chen, H., Eds. *Proceedings of the 50-year Teaching and Research Anniversary of Prof Sun Wei on Advances in Civil Engineering Materials*, RILEM Publications SARL, 191-200.
- Mackenzie, J., (1950). "The elastic constants of a solid containing spherical holes." *Proceedings of the Physical Society Section B*, 63, 2.
- Macphee, D. E., Luke, K., Glasser, F. P. and Lachowski, E. E., (1989). "Solubility and aging of calcium silicate hydrates in alkaline solutions at 25 °C." *Journal of the American Ceramic Society*, 72, 646-654.
- Mendoza, O., Giraldo, C., Camargo, S. S. and Tobón, J. I., (2015). "Structural and nano-mechanical properties of Calcium Silicate Hydrate (CSH) formed from alite hydration in the presence of sodium and potassium hydroxide." *Cement and Concrete Research*, 74, 88-94.
- Mo, X., (2005). "Laboratory study of LiOH in inhibiting alkali-silica reaction at 20°C: a contribution." *Cement and Concrete Research*, 35, 499-504.
- Mota Gassó, B., (2015). "Impact of alkali salts on the kinetics and microstructural development of cementitious systems." Thesis (PhD). École Polytechnique Fédérale de Lausanne.
- Myers, R. J., Bernal, S. A. and Provis, J. L., (2014). "A thermodynamic model for C-(N-) ASH gel: CNASH_{ss}. Derivation and validation." *Cement and Concrete Research*, 66, 27-47.
- NocuŃ-Wczelik, W., (1999). "Effect of Na and Al on the phase composition and morphology of autoclaved calcium silicate hydrates." *Cement and Concrete Research*, 29, 1759-1767.
- Provis, J. L., Palomo, A. and Shi, C., (2015). "Advances in understanding alkali-activated materials." *Cement and Concrete Research*, 78, 110-125.
- Provis, J. L. and Van Deventer, J. S. J., (2009). "Geopolymers: structures, processing, properties and industrial applications." Elsevier.
- Rajabipour, F., Giannini, E., Dunant, C., Ideker, J. H. and Thomas, M. D., (2015). "Alkali-silica reaction: Current understanding of the reaction mechanisms and the knowledge gaps." *Cement and Concrete Research*, 76, 130-146.
- Richardson, I., (1999). "The nature of CSH in hardened cements." *Cement and Concrete Research*, 29, 1131-1147.
- Richardson, I., Brough, A., Groves, G. and Dobson, C., (1994). "The characterization of hardened alkali-activated blast-furnace slag pastes and the nature of the calcium silicate hydrate (CSH) phase." *Cement and Concrete Research*, 24, 813-829.
- Sant, G., Kumar, A., Patapy, C., Le Saout, G. and Scrivener, K., (2012). "The influence of sodium and potassium hydroxide on volume changes in cementitious materials." *Cement and Concrete Research*, 42, 1447-1455.
- Shi, C., Roy, D. and Krivenko, P., (2006). "Alkali-activated cements and concretes." CRC press.
- Skibsted, J. and Andersen, M. D., (2013). "The effect of alkali ions on the incorporation of aluminum in the calcium silicate hydrate (C-S-H) phase resulting from Portland cement hydration studied by ²⁹Si MAS NMR." *Journal of the American Ceramic Society*, 96, 651-656.
- Stade, H., (1989). "On the reaction of CSH (di, poly) with alkali hydroxides." *Cement and Concrete Research*, 19, 802-810.
- Taylor, H. F., (1987). "A method for predicting alkali ion concentrations in cement pore solutions." *Advances in Cement Research*, 1, 5-17.
- Taylor, H. F., (1997) "Cement chemistry." Thomas Telford.
- Thomas, J. J., Jennings, H. M. and Allen, A. J., (1998). "The surface area of cement paste as measured by neutron scattering: evidence for two CSH morphologies." *Cement and Concrete Research*, 28, 897-905.
- Thomas, M. D. A., (2001). "The role of calcium hydroxide in alkali recycling in concrete." In: Skalny, J., Gebauer, J. and Odler, I. (Eds.) *Materials Science of Concrete Special volume*, American Ceramic Society, Westerville, OH, USA, 225-236.
- Thomas, R. J., Ye, H., Radlińska, A. and Peethamparan,

- S., (2016). "Alkali-activated slag concrete: A closer look at sustainable alternatives to portland cement." *Concrete International*, 38, 33-38.
- Viallis, H., Faucon, P., Petit, J.-C. and Nonat, A., (1999). "Interaction between salts (NaCl, CsCl) and calcium silicate hydrates (CSH)." *The Journal of Physical Chemistry B*, 103, 5212-5219.
- Wittmann, F., (1973). "Interaction of hardened cement paste and water." *Journal of the American Ceramic Society*, 56, 409-415.
- Ye, H., (2015). "Creep mechanisms of calcium-silicate-hydrate: An overview of recent advances and challenges." In: *International Journal of Concrete Structures and Materials*, 9, 453-462.
- Ye, H., Cartwright, C., Rajabipour, F. and Radlińska, A., (2014). "Effect of drying rate on shrinkage of alkali-activated slag cements." In: *Proceedings of the 4th International Conference on the Durability of Concrete Structure (ICDCS)*. 24-26 July 2014, Purdue University, Indiana, USA, 254-261.
- Ye, H., Cartwright, C., Rajabipour, F. and Radlińska, A., (2017a). "Understanding the drying shrinkage performance of alkali-activated slag mortars." *Cement and Concrete Composites*, 76, 13-24.
- Ye, H. and Radlińska, A., (2016a). "Fly ash-slag interaction during alkaline activation: Influence of activators on phase assemblage and microstructure formation." *Construction and Building Materials*, 122, 594-606.
- Ye, H. and Radlińska, A., (2016b). "Quantitative analysis of phase assemblage and chemical shrinkage of alkali-activated slag." *Journal of Advanced Concrete Technology*, 14, 245-260.
- Ye, H. and Radlińska, A., (2016c). "Shrinkage mechanisms of alkali-activated slag." *Cement and Concrete Research*, 88, 126-135.
- Ye, H., Radlińska, A. and Neves, J., (2017b). "Drying and carbonation shrinkage of cement paste containing alkalis." *Materials and Structures*, 50, 132.