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Modified model of alkali-silica reaction

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Abstract

Experimental studies have been carried out for understanding why soft and fluid hydrated alkali silicate generated by the alkali–silica reaction (ASR) of aggregate with alkaline pore solution accumulates the expansive pressure for cracking the aggregate and the surrounding concrete. The elemental analysis of aggregate (andesite) embedded in a cement paste has revealed that the alkali silicate has no ability of generating expansive pressure unless the aggregate is tightly packed with a reaction rim. The reaction rim is slowly generated from the alkali silicate that covers the ASR-affected aggregate. Consumption of alkali hydroxide by the ASR induces the dissolution of Ca^{2+} ions into the pore solution. The alkali silicate then reacts with Ca^{+} ions to convert to an insoluble tight and rigid reaction rim. The reaction rim allows the penetration of alkaline solution but prevents the leakage of viscous alkali silicate, so that the alkali silicate generated afterward by the ASR is accumulated in the aggregate to give an expansive pressure enough for cracking the aggregate and the surrounding concrete. The ASR of very tiny aggregate such as fly ash and municipal waste incinerator bottom ash may not cause the deterioration of concrete, since the ASR is completed before the formation of reaction rims.

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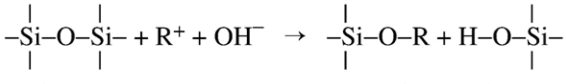
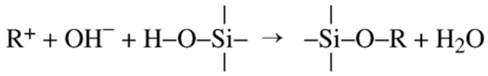
1. Introduction

Alkali-silica reaction in concrete (ASR) is the reaction of silica-rich aggregates with an alkaline solution in the micro pores of concrete, and is one of main chemical reactions causing slow but severe deterioration of concrete structures [1]. The first step of the ASR is the scission of siloxane networks in aggregates by OH^- ions to generate alkali silicate and silicic acid [2],



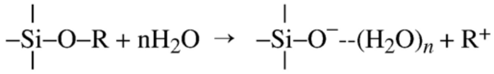
$$-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + R^+ + OH^- \rightarrow -\overset{|}{\underset{|}{Si}}-O-R + H-O-\overset{|}{\underset{|}{Si}}-$$

where R^+ denotes an alkali ion such as Na^+ and K^+. The silicic acid is a weak acid, so that it immediately reacts with OH^- to convert to alkali silicate,



$$R^+ + OH^- + H-O-\overset{|}{\underset{|}{Si}}- \rightarrow -\overset{|}{\underset{|}{Si}}-O-R + H_2O$$

The resultant oligomeric alkali silicate (alkali silicate gel) is hygroscopic except for R = Li, so that it is expanded by the hydration,



$$-\overset{|}{\underset{|}{Si}}-O-R + nH_2O \rightarrow -\overset{|}{\underset{|}{Si}}-O^-\text{--}(H_2O)_n + R^+$$

where *n* denotes the hydration number of the silicate anion. The expansive pressure generated by these reactions induces the cracking of the aggregate and surrounding concrete, which causes the deterioration of concrete.

Although the cracking of concrete by hydrated alkali silicate has been widely accepted, it is still unclear how the soft and fluid hydrated gel causes the cracking of concrete [3,4]. Based on the observation that the cracks in ASR-affected concrete are filled with minerals generated from the hydrated gel, Dron and Brivot [5] proposed that the hydrated gel is diffused far from the aggregate into micro pores and channels connecting the pores. The gel then reacts with Ca^{2+} ions and expands to induce the cracking of concrete. However it is not clear

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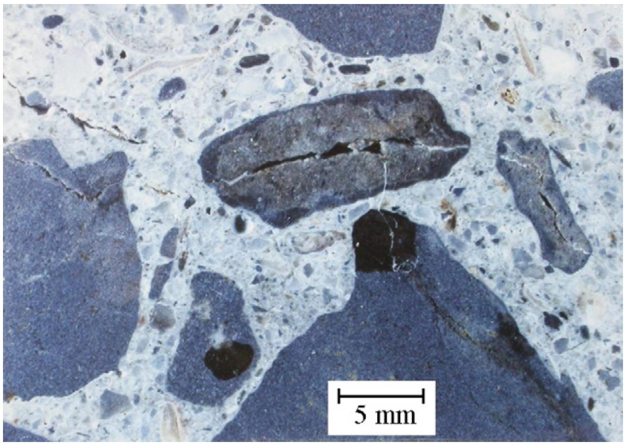


Fig. 1. Typical crack pattern in ASR-affected field concrete containing andesite as main aggregates.

why the gel generates an expansive pressure in the pores. In addition, their model can not predict the cracking of the aggregate itself, since the expansion gives a compressive pressure to the aggregate.

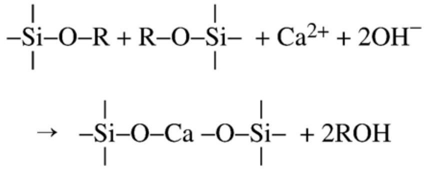
Bažant and Steffens [6] proposed that the cracking of concrete is induced by the expansive pressure accumulated in the boundary region between the aggregate and surrounding cement paste. The expansive pressure is initially released by pushing the hydrated gel into accessible micro pores near the surface of the aggregate. Once the pores around the aggregate are completely filled with the hydrated gel, further formation of the hydrated gel causes the accumulation of the expansive pressure between the cement past and the unaffected aggregate core. The expansive pressure is finally released by cracking the cement paste. According to their model, the cracking of the cement past should not accompany the cracking of the aggregate, since the expansive pressure exerts a compressive pressure to the aggregate.

Based on the analysis of crack patterns in ASR-affected concrete, many researchers including Idorn [7] and Goltermann [8] concluded that the expansive pressure due to the formation of hydrated gel is accumulated inside the reacting aggregate. The aggregate expands inhomogeneously through the ASR, which causes tension in the aggregate. The release of the expansive pressure therefore causes the crack of both the aggregate and surrounding cement paste.

Based on the analysis of crack patterns and the elemental and hardness mappings of ASR-affected aggregates in field concrete, we proposed a modified mechanism of ASR [9,10] in which a reaction rim generated around the ASR-affected aggregate plays a significant role in the deterioration of concrete. Since the original papers are written in Japanese, the outline of our model will be briefly mentioned.

Fig. 1 shows the cross section of a field concrete that is affected by ASR. The crack seems to be developed by utilizing ASR-affected aggregates as stepping stones, which implies that the expansive pressure was accumulated in the aggregates.

As shown in Fig. 2 (and also in Fig. 1), the ASR-affected aggregate shows a dense and dark reaction rim that is generated by the reaction of alkali silicate and calcium ions as



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\mathrm{R}+\mathrm{R}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}-\ +\mathrm{Ca}^{2+}+2\mathrm{OH}^{-}$$
$$\rightarrow\ -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\mathrm{Ca}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}-\ +2\mathrm{ROH}$$

As shown in Table 1, the reaction rim is harder and therefore denser than the surrounding cement paste and the ASR-affected inner aggregate, so that the reaction rim gives a more smooth surface than the surroundings after polishing for observation. A smooth surface looks darker because it reflects less light than a rough surface.

These evidences suggest that the reaction rim acts as a semi-permeable hard membrane that allows the penetration of not the alkali silicate gel but the alkaline solution and therefore keeps the expansive pressure in the reacting aggregate. The accumulated pressure cracks the aggregate and the surrounding cement paste when the pressure exceeds the tolerance of the aggregate surrounded by the reaction rim and the cement paste. Formation of the crack in the cement past reduces the compressive pressure for nearby pre-cracked aggregates, which triggers the cracking of nearby aggregates.

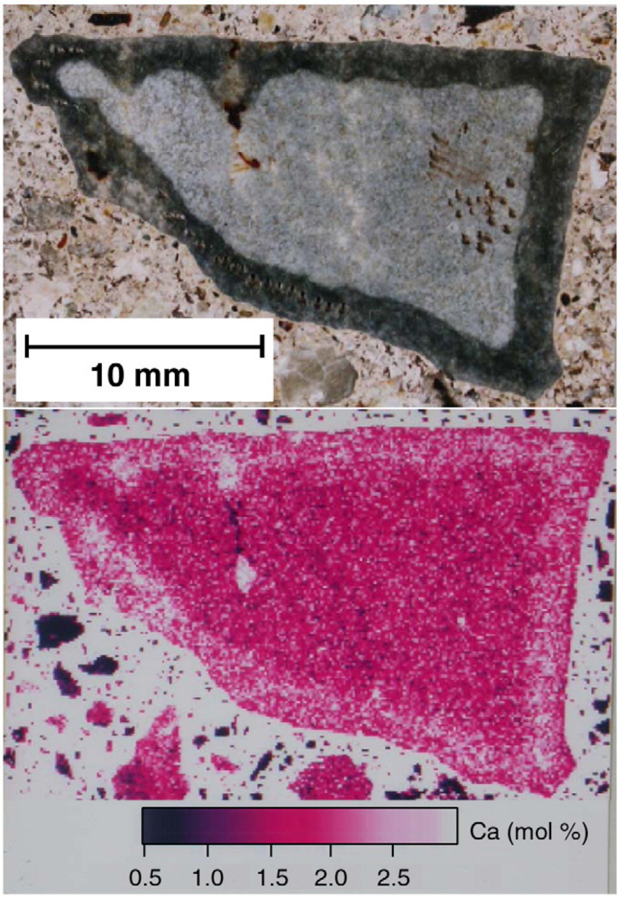


Fig. 2. Cross section (top) and its false color elemental mapping of calcium (bottom) for ASR-affected andesite. See the online version for the full color image.

Table 1
Vickers hardness of andesite [a]

Location	Reaction rim	Inside of the rim
Average hardness	294	190
Deviation	±20	±23

[a] The original Vickers hardness of andesite is 412.

The proposed model is based on the following three assumptions that should be proved to be valid;

1) The reaction rim is generated by the reaction of Ca^+ with fluid hydrated alkali silicate that covers the surface region of the aggregate, so that the reaction rim has no hole to allow the leakage of hydrated gel that is generated after the formation of the reaction rim.
2) The reaction rim acts as a semi-permeable hard membrane to allow the penetration of alkaline solution into the aggregate.
3) The reaction rim is hard enough to accumulate the expansive pressure necessary for cracking the aggregate.

The present study is aimed at proving the validity of these assumptions.

2. Experimental

The sample used for studying the mechanism of reaction rim formation was composed of portland cement and ASR-reactive andesite containing significant amount of glassy silicate. Table 2 shows the average contents of main elements in the cement and the andesite that were measured with an electron probe micro analyzer. A 1 cm × 1 cm × 10 cm bar of the andesite was embedded at the center of a 10 cm × 10 cm × 10 cm concrete block composed of the cement and water of 1 : 0.5 weight ratio. For accelerating the ASR, the content of alkali was enriched to 2.5 times while keeping the Na_2O/K_2O ratio constant. The concrete block wrapped with a cloth was kept at 313 K under 100% relative humidity for 4 months. The concrete block was then kept in a closed plastic bag at room temperature. Test pieces of 10 cm × 10 cm × 2 cm with 1 cm × 1 cm × 2 cm andesite at the center were obtained by cutting the block at 2 cm from the surface of the block at 1 month, 2 months, 4 months and 3 years after the preparation. The fresh surface of the pieces was polished by using diamond paste as a final abrasive. The distribution of Si, Al, Fe, Ca, Mg, Na, K, Ti and Mn atoms were then measured by using the electron probe micro analyzer.

For clarifying the role of reaction rim in the crack of aggregates, hard glass beads (diameter: 5 mm) as a model material of aggregate were immersed in an aqueous solution of 0.1 mol/dm^3 NaOH and a saturated aqueous solution of $Ca(OH)_2$. The temperature of the solutions was kept at 353 K for accelerating chemical reactions.

3. Results and Discussion

3.1. Accelerated test

Fig. 3 shows the distribution of S, Si and Ca near the boundary of andesite and the cement paste at four months and three years after the preparation of the concrete block. The distribution at two months after the preparation was approximately the same as that at 4 months, which implies that the accelerated ASR ceased within two months. Since the original concentrations of Na and K atoms in the aggregate were too high to detect the migration of alkaline pore solution from the cement past to the aggregate, the S atom dissolved in the alkaline solution as SO_4^{2-} was mapped for detecting the penetration of the solution into the aggregate. As shown in the upper part of Fig. 3, the penetration of alkaline solution from the cement past causes the transfer of resultant hydrated alkali silicate form the aggregate to the cement past. The thickness of the Si-depleted region is approximately the same as that of the Si-enriched region, which indicates free migration of the alkali silicate and therefore no formation of expansive pressure. Although a Ca-rich region corresponding to the reaction rim is too thin to be observed at 4 months after the preparation, it is observed after keeping the concrete bar for three years. These results support our proposed model that the reaction rim is generated by the reaction of fluid hydrated alkali silicate with Ca^{2+} ions that is dissolved from the cement paste due to the decrease of OH^- ions by the ASR. The delayed formation of the reaction rim can be explained as follows.

The concentration of ions in a solution is determined by the solubility of the least soluble solid that can be precipitated from the solution, so that the concentration of Ca^{2+} ions in the alkaline solution is given by $[Ca^{2+}] = 4.8 \times 10^{-5}/[OH^-]^2$, where 4.8×10^{-5} is the solubility product at room temperature, and $[Ca^{2+}]$ and $[OH^-]$ are the concentrations of Ca^{2+} and OH^-in mol/dm^3, respectively. Suppose $[OH^-]$ in the alkaline solution is 0.1 mol/dm^3 (pH = 13), the concentration of Ca^{2+} ions is only 0.0048 mol/dm^3. The alkaline solution therefore contain Ca^{2+} ions that is not enough for generating a hard reaction rim composed of −O−Si−O−Ca−O−Si−O− networks.

The consumption of R^+ and OH^- ions by the formation of alkali silicate decreases the concentration of OH^- ions in the cement paste surrounding the aggregate, which leads to the increase of Ca^{2+} ions in the solution [11]. The fluid and therefore homogeneous alkali silicate surrounding the ASR-affected aggregate is then gradually converted to a hard reaction rim that is dense enough for preventing the leakage of fluid alkali silicate gel generated after the formation of the reaction rim.

Formation of alkali silicate after the formation of the reaction rim necessitates the penetration of the alkaline solution through the reaction rim into the aggregate. Although the penetration was not detected in the present study, Rivard *et al.* [12] have detected the penetration of NaOH and KOH through the reaction rim of ASR-affected Potsdam sandstone .

Table 2
Chemical composition (wt.%) of cement and andesite

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	TiO_2	MgO	SO_3
Cement	20.8	5.1	3.2	63.6	0.5	1.5		1.5	2.8
Andesite	70.3	11.2	2.5	0.7	1.2	7.5	1.1		

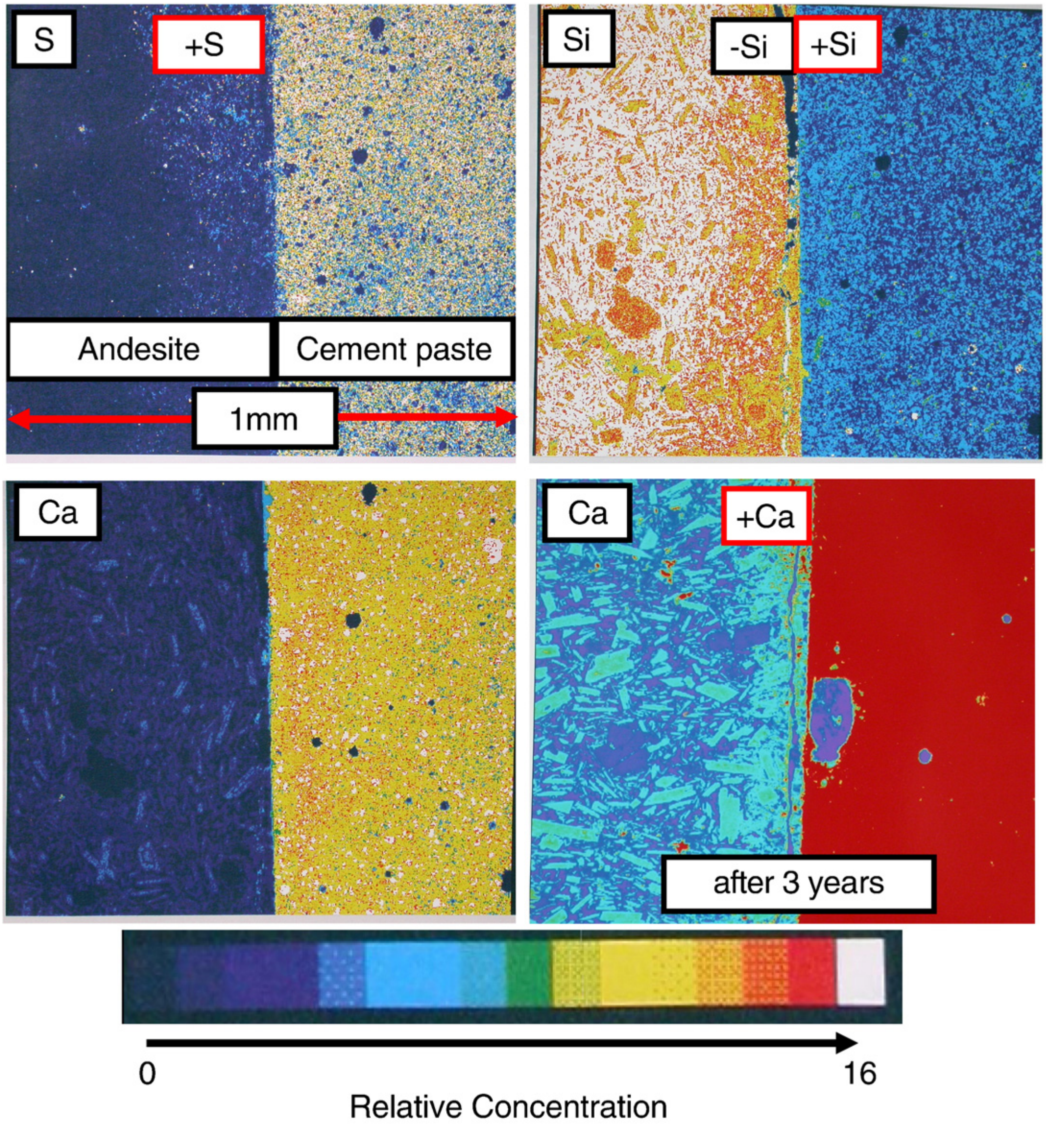


Fig. 3. False color elemental mappings of sulfur, silicon and calcium near the boundary of andesite and cement paste at four months after the preparation of concrete $\boxed{+X}$ and $\boxed{-X}$ show the zones where element X is increased and decreased after the preparation, respectively. The map at the bottom right was observed at three years after the preparation. The concentrations of Ca at four months and at three yeas are essentially the same except for the boundary layer, but the scales for the mappings are different. See the online version for the full color image.

3.2. Glass beads in alkaline solutions

The role of reaction rim in the crack formation was examined by immersing hard glass beads (diameter: 5 mm) into an aqueous solution of 0.1 mol/dm^3 NaOH and a saturated aqueous solution of $Ca(OH)_2$. As summarized in Table 3, three of five glass beads were cracked by immersing in the solutions only in the order of NaOH, $Ca(OH)_2$ and then NaOH. Repeated plunging of the glass beads at 295 K into boiled water did not crack the beads, which certifies that the crack was generated not by the thermal shock but by chemical reactions. Cracking of the glass beads by immersing in the solutions indicates that the reaction rim with enough thickness for accumulating the expansive pressure for cracking the bead is generated by the reaction of Ca^{2+} ions with preexisting alkali silicate, and the NaOH solution can penetrate through the reaction rim into the glass bead to generate the expansive pressure by producing new hydrated alkali silicate.

The experimental result summarized in Table 3 can be explained as follows;

Penetration of the $Ca(OH)_2$ solution into a glass bead does not generate an expansive pressure, since the resultant rigid calcium silicate or calcium alkali silicate is water-insoluble and is not swollen by absorbing water [7,13]. Therefore, the immersion of a glass bead in the $Ca(OH)_2$ solution does not generate an expansive pressure enough for cracking the bead.

Immersion of a glass bead in the NaOH solution changes the surface layer of the bead into soft alkali silicate that can expand and is partially dissolved into the solution to accumulate no expansive pressure.

Immersion of a glass bead into the mixed solution of NaOH and $Ca(OH)_2$ generates a thin and rough reaction rim that can not

Table 3
Effect of chemical treatments on the crack of hard glass bead

	5 days	5 days	5 days	5 days	2 days	2 days
First treatment	Ca $(OH)_2$ [a]	NaOH [b]	NaOH + Ca $(OH)_2$ [c]	Ca $(OH)_2$	NaOH	NaOH
Second treatment				NaOH	Ca $(OH)_2$	Ca $(OH)_2$
				5 days	5 days	3 days
Third treatment					water	NaOH
					3 days	1 days
Number of cracked beads [d]	0/5	0/5	0/5	0/5	0/5	3/5

[a] Saturated aqueous solution of $Ca(OH)_2$ at 353 K.
[b] Aqueous solution of 0.1 mol/dm^3 NaOH at 353 K.
[c] 10:1 mixture of the NaOH and the $Ca(OH)_2$ solutions.
[d] Number of cracked beads within five tested beads.

act as a reaction rim with the strength enough for accumulating the expansive pressure generated by the formation of hydrated alkali silicate. Based on the observation that the reaction of alkali ions with flint aggregate precedes the reaction of Ca^{2+} ions [14], Khouchaf *et al.* [15] measured the elemental maps of the aggregate that was ASR-affected by immersing it at 353 K in a 0.79 mol/dm^3 KOH solution containing $Ca(OH)_2$ powder ($[Ca^{2+}] = 7.7 \times 10^{-5}$ mol/dm^3). They found that the ASR-affected grain is covered with a Ca-rich rough film of a few μm thickness through which K^+ ions diffuses inside the grain. Although they assumed that the Ca-rich film is directly generated by the reaction of flint, Ca^{2+} and OH^-, comparison of the elemental maps of Ca, Si and O clearly indicates that the Ca-rich film is generated by the reaction of Ca^{2+} ions and fluid alkali silicate that is partially peeled off from the grain. A thin and rough Ca-rich film can not prevent the leakage of the hydrated alkali silicate from the glass bead, so that no glass bead is cracked in the mixed solution of NaOH and CaOH.

The formation of calcium silicate by the direct reaction of silicate and the $Ca(OH)_2$ solution is so slow [16] that the resultant reaction rim may be too thin to keep the hydrated alkali silicate inside of the reaction rim. The alkali silicate generated afterward by immersing the bead in the NaOH solution destroys the thin reaction rim to release the expansive pressure.

Immersing a glass bead in the $Ca(OH)_2$ solution after immersing it in the NaOH solution induces the fast conversion of a soft alkali silicate layer around the bead into hard calcium alkali silicate [17,18], so that the resultant reaction rim has enough thickness for keeping the expansive pressure generated afterward by the formation of new alkali silicate. The successive immersion in the NaOH, $Ca(OH)_2$ and NaOH solutions thereby cracks the glass bead.

Fig. 4 shows the cross section of a cracked bead. The cracks are penetrated deep into the bead, which suggests the presence of local strain due to spatially inhomogeneous ASR under the reaction rim.

3.3. Origin of expansive pressure

It is evident from the experimental results that the reaction rim acts as a semi-permeable hard membrane that allows the penetration of alkali hydroxide into the aggregate but prevents the extrusion of the resultant expansive hydrated alkali silicate outside of the aggregate. The expansive pressure is thereby gradually accumulated in the aggregate after the formation of the reaction rim. The reaction rim is concomitantly thickened to torelate the increasing expansive pressure. We estimate here the amount of the expansive pressure accumulated under the reaction rim. The expansive pressure generated by the ASR is generally believed to be an osmotic pressure that is generated by the difference between the mole fractions of water inside and outside of the membrane (reaction rim). The osmotic pressure is therefore not responsible for the expansive pressure when the pore solution dissolves enough amount of alkali silicate that is extruded from the aggregate before the formation of the reaction rim. Based on the DLVO theory, Prezzi *et al.* [19] claimed that the expansive pressure arises from the double layer force that is generated by the overlap of diffuse electrical double layers around charged particles. However, our rigorous treatment of the DLVO theory [20] indicated that the double layer force is negligible in hydrated alkali silicate composed of mobile positive and negative ions.

The highest and therefore the most important pressure is the chemical pressure that has not been rigorously treated in explaining the deterioration of concrete by the ASR. As suggested by Garcia-Diaz *et al*. [21], the chemical pressure is generated by the expansion of the volume of aggregates by chemical reactions. Chemical reactions taking place between an alkaline solution and a siliceous aggregate through a reaction rim are the scission of siloxane networks by OH^- ions followed by the hydration of resultant alkali silicate, as

$$2R^+ + 2OH^- + x\mathrm{SiO2} \rightarrow R_2Si_xO_{2x+1} + H_2O \tag{1}$$

$$R_2Si_xO_{2x+1} + (2m+n)H_2O \rightarrow 2[R^+-(H_2O)_m] + Si_xO_{2x+1}^{2-}-(H_2O)_n \tag{2}$$

where m and n are hydration numbers of R^+ cation and silicate anion, respectively. Since the reactions at atmospheric pressure causes the increase of the volume of the reactant, the pressure in the aggregate gradually increases as the reactions proceed.

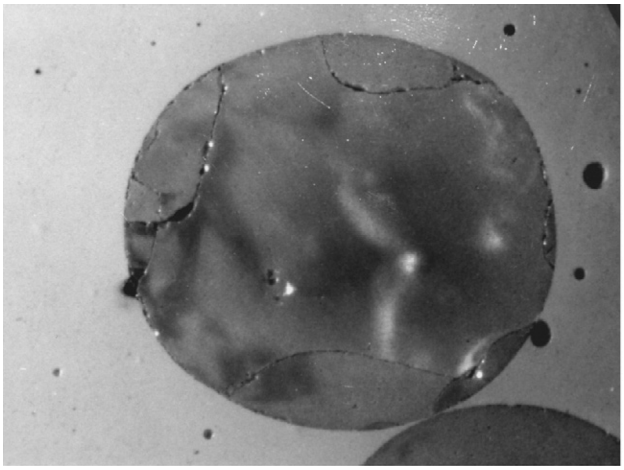


Fig. 4. Cross section of cracked hard glass bead.

Increase of the pressure causes increase of the chemical potentials of the species in the right sides of the above equations. The reactions are terminated when the pressure becomes high enough for equalizing the chemical potentials of the right and left side species. The system then reaches an equilibrium state.

The pressure under the equilibrium can be estimated by calculating the pressure dependence of the Gibbs free energy of the alkali silicate. The Gibbs free energy $G(P,T_0)$ at pressure P and standard temperature T_0 (=298 K) is related to the molar volume $V(P,T_0)$ and the free energy $G(P_0,T_0)$ at standard pressure P_0 ($=1.013\times10^5$ Pa) through the fundamental thermodynamic relation of

$$\frac{\partial G(P,T_0)}{\partial P} = V(P,T_0) \tag{3}$$

The pressure is related to the volume through the compressibility κ as

$$\kappa = -\frac{1}{V(P,T_0)}\frac{\partial V(P,T_0)}{\partial P} \tag{4}$$

Integration of Eq. (4) gives

$$V(P,T_0) = V(P_0,T_0)\exp[-\kappa(P-P_0)] \tag{5}$$

Integration of Eq. (3) after substitution of Eq. (5) gives

$$\begin{aligned}\int_{P_0}^{P}\frac{\partial G(P,T_0)}{\partial P}\mathrm{d}P &= G(P,T_0) - G(P_0,T_0)\\ &= \frac{1}{\kappa}V(P_0,T_0)\{1-\exp[-\kappa(P-P_0)]\}\end{aligned} \tag{6}$$

The free energy of the system at pressure P is larger than that under the standard condition by $V(P_0,T_0)\{1-\exp[-\kappa(P-P_0)]\}/\kappa$. The alkali–silica reaction stops at pressure $P_{\max}$ where the free energy change of the reactions becomes zero, so that

$$-\boldsymbol{\Delta}G(P_0,T_0) = \frac{1}{\kappa}V(P_0,T_0)\{1-\exp[-\kappa(P_{\max}-P_0)]\} \tag{7}$$

Expansion of Eq. (7) leads

$$P_{\max} = P_0 - \frac{1}{\kappa}\log\left[1+\frac{\kappa\boldsymbol{\Delta}G(P_0,T_0)}{V(P_0,T_0)}\right] \tag{8}$$

The compressibility of condensed inorganic materials lies between 10^{-10} and 10^{-11}. Assuming $\Delta G(P_0,T_0)/V(P_0,T_0)\ll 1/\kappa$ and using an approximation of $\log(1+x)\approx x$ for $|x|\ll 1$, Eq. (8) is simplified as

$$P_{\max} = P_0 - \frac{\boldsymbol{\Delta}G(P_0,T_0)}{V(P_0,T_0)} \tag{9}$$

Suppose an aggregate SiO_2 of density = 2.6 reacts with a NaOH solution to convert to $Na_2Si_2O_5(H_2O)_{8.4}$ of density = 1.6 [22], the Gibbs free energy for the reaction is estimated from the free energies of

$$2Na + 2Si + (5/2)O_2 = Na_2Si_2O_5 - 2322\ \mathrm{kJ/mol} \tag{10}$$

$$2SiO_2 - 2\times 856.6\ \mathrm{kJ/mol} = 2Si + 2O_2 \tag{11}$$

$$2NaOH - 2\times 379.5\ \mathrm{kJ/mol} = 2Na + O_2 + H_2 \tag{12}$$

$$H_2 + (1/2)O_2 = H_2O - 237.1\mathrm{kJ/mol} \tag{13}$$

$$2Na^+ + 2OH^- + 2\times \Delta G_{Na^+} + 2\times \Delta G_{OH^-} = 2NaOH \tag{14}$$

$$Na_2Si_2O_5 = 2Na^+ + Si_2O_5^{2-} + 2\times \Delta G_{Na^+} + \Delta G_{Si_2O_5^{2-}} \tag{15}$$

as

$$\begin{aligned}2SiO_2 + 2Na^+ + 2OH^- = {}& Si_2O_5^{2-} + 2Na^+ + H_2O\\ &+ \Delta G_{Si_2O_5^{2-}} - 2\times\Delta G_{OH^-}\\ &- 86.9\mathrm{kJ/mol}\end{aligned} \tag{16}$$

Here Na^+, OH^- and $Si_2O_5^{2-}$ denote hydrated ionic species, and ΔG_{Na^+}, ΔG_{OH^-} and $\Delta G_{Si_2O_5^{2-}}$ are free energies for the formation of these species. The hydration energy of negative ions is generally much lower than that of positive ions. Although the values of ΔG^{-}_{OH} and ΔG^{2-}_{Si2O5} are not known, assuming $\Delta G^{2-}_{Si2O5} = 2\times\Delta G^{-}_{OH}$, the Gibbs free energy for the formation of hydrated alkali silicate from silica is estimated to be −86. 9 kJ/mol. The value of $V(P_0,T_0)$ is estimated from the molecular weight and the density $Na_2Si_2O_5(H_2O)_{8.4}$ to be 208×10^{-6} m^3/mol, so that the value of $\kappa\Delta G(P_0,T_0)/V(P_0,T_0)$ is much smaller than unity. The maximum pressure is then estimated from Eq. (9) to be $P_{\max}\approx 4\times10^8$ Pa. The expansive pressure generated by the chemical reactions is two orders of magnitude higher than that for the deterioration [23].

4. Conclusion

Fig. 5 shows the schematic representation of our proposed mechanism of the ASR-induced deterioration of concrete. The deterioration proceeds according to the following steps;

1) OH^- and R^+ ions in the pore solution de-polymerize silica-rich aggregates to convert to fluid hydrated alkali silicate. The surface region of the aggregate is homogeneously covered with the alkali silicate. Consumption of OH^- ions by the reaction assists the dissolution of Ca^{2+} ions into the solution.
2) The Ca_2^+ ions easily penetrate into the soft alkali silicate to re-polymerize the silicate. The aggregate is now tightly packed with a rigid reaction rim that allows the penetration of not alkali silicate but R^+, Ca^{2+} and OH^- ions. The Ca^{2+} ions penetrate much slower than the R^+ ions.

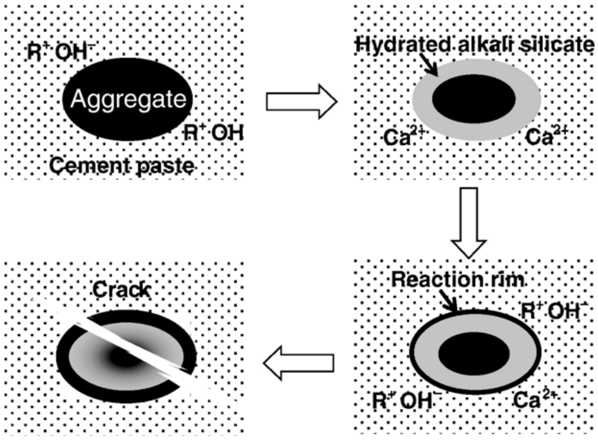


Fig. 5. Schematic representation of the mechanism of ASR-induced cracking of concrete.

3) The OH^- and R^+ ions penetrate through the reaction rim to convert the fresh silicate into bulky alkali silicate. The resultant expansive pressure is stored in the aggregate. The accumulated pressure cracks the aggregate and the surrounding cement paste when the pressure exceeds the tolerance of the aggregate surrounded by the reaction rim and the cement paste.

Our model claims that the ASR does not cause the deterioration of concrete, if the ASR is completed before the formation of the reaction rim. Reactive but tiny silica-rich aggregate such as fly ash and municipal waste incinerator bottom ash do not induce the deterioration of concrete, since they are completely converted to alkali silicate before the formation of reaction rims. They rather act as pozzolanic materials [24,25] since they absorb alkali ions and therefore reduce the concentration of R^+ and OH^- ions.

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