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# Alkali–silica reaction, pessimum effects and pozzolanic effect

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ABSTRACT

The pessimum proportion and pessimum size effects for alkali–silica reaction-induced deterioration of concrete (ASR) and the pozzolanic effect of fine siliceous admixtures in concrete have been explained based on the proposed ASR model [T. Ichikawa, M. Miura, Modified model of alkali–silica reaction, Cem. Concr. Res. 37 (2007) 1291–1297.]. The attack of alkali hydroxide to aggregate particles composed of ASR-reactive minerals generates the layer of hydrated mature alkali silicate and the layer of less hydrated immature alkali silicate under the mature layer. The mature alkali silicate preferentially reacts with $Ca^{2+}$ ions to convert to fragmental calcium alkali silicate, because the reaction accompanies a significant volume contraction. The immature alkali silicate gradually reacts with $Ca^{2+}$ ions to cover the surface of the reactive minerals with tight layers of calcium alkali silicate called reaction rims. The reaction rims allow the penetration of alkaline solution but prevents the leakage of viscous alkali silicate generated afterward, so that the alkali silicate is accumulated inside the rims to give an expansive pressure enough for cracking the aggregate and the surrounding concrete. Due to the absorption of $Ca^{2+}$ ions by mature alkali silicate, too much increase of the proportion of reactive aggregate causes the deficiency of $Ca^{2+}$ ions for the formation of reaction rims, so that the ASR expansion decreases after passing the pessimum proportion. Very fine reactive aggregate and admixtures with the grain size less than ~50 μm preferentially react with alkali hydroxide to convert to mature alkali silicate without leaving any reactive minerals. Homogeneous mixing of the sufficient amount of very fine siliceous admixtures in concrete therefore inhibits the ASR by absorbing $Ca^{2+}$ ions for the rim formation. The resultant fragmental calcium silicate fills the pores in concrete to increase the strength and the durability of the concrete. The admixtures thus act as pozzolanic materials.

## 1. Introduction

Alkali–silica reaction in concrete (ASR) is one of the main chemical reactions causing gradual but severe deterioration of hardened concrete structures [1]. ASR is a reaction between reactive silica in concrete aggregates and an alkaline solution in the micro pores of concrete, which results in the formation of bulky hydrated alkali silicate gel. The expansive pressure generated by the hydrated alkali silicate has been widely believed to induce the cracking and deterioration of concrete. However it is not necessarily correct. Concrete is a porous material and the hydrated alkali silicate is rheologically a fluid material, so that the hydrated alkali silicate slowly diffuses into the pores and preexisting cracks to loose its expansive pressure. The diffused alkali silicate was proposed to generate an expansive pressure by reacting with $Ca^{2+}$ ions [2]. The resultant solid calcium silicate generally contains certain amount of alkali ions, so that we hereafter call it calcium alkali silicate. The calcium alkali silicate is, however, impossible to generate any expansive pressure since the reaction causes the shrinkage of the silicate by the release of alkali ions and hydration water. The hygroscopisity of the resultant calcium alkali silicate is much lower than that of alkali silicate. The reaction of $Ca^{2+}$ ions with alkali silicate is a cross-linking reaction which converts two independent bonds to one bond, so that the volume of the calcium alkali silicate is much smaller than that of alkali silicate.

One might assume that the hydrated alkali silicate cannot penetrate into the surrounding pores but is accumulated around the aggregates to generate an expansive pressure [3]. However this model cannot explain the observed cracking of ASR-affected aggregates, since the expansion of surrounding alkali silicate exerts a compressive pressure to prevent the cracking of the aggregates. The ASR-affected aggregates are generally cracked and expanded due to the accumulation of expansive pressure within the aggregates [4,5].

It is well known that both $Ca(OH)_2$ and high $OH^-$ ion concentration are necessary for concrete expansion by ASR [6–13], but their role has not been widely understood. Based on the analysis of crack patterns and the elemental and hardness mappings of ASR-affected aggregates in field concrete, Dr. Miura and the present author proposed a new ASR model in 1996 in which alkali hydroxide and $Ca^{2+}$ ions successively attack reactive aggregate to induce the ASR [13]. The first step of the ASR is the attack of alkali hydroxide to convert the surface layer of the aggregate to alkali silicate. The consumption of $OH^-$ ions induces gradual dissolution of $Ca^{2+}$ ions from $Ca(OH)_2$ into the pore solution, because the concentration of $Ca^{2+}$

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ions is inversely proportional to the square of $OH^-$ concentration. The alkali silicate layer reacts with the $Ca^{2+}$ ions to form a hard and tight reaction rim composed of calcium alkali silicate. The reaction rim allows the penetration of alkaline solution into the aggregate but not the extrusion of viscous hydrated alkali silicate from the aggregate. The alkali silicate newly formed in the aggregate is therefore compressed to generate an expansive pressure that is enough for cracking the rim and the surrounding cement paste. The validity of the proposed model was confirmed by a concrete prism test using andesite as a reactive aggregate and chemical tests using hard glass beads as model aggregate and 0.1 N solution of NaOH and saturated $Ca(OH)_2$ solution as model pore solutions [14,15].

One of the features of ASR that has not been understood is the effect of the proportion and the size of reactive aggregate on the ASR-induced expansion of concrete. Stanton demonstrated in 1940 that a certain proportion of some reactive siliceous aggregate caused the largest expansion of concrete, and that the expansion decreased when the content of the reactive aggregate in the concrete was increased or decreased from that pessimum proportion [16]. He also found that, for a fixed proportion of reactive aggregate, the expansion became the maximum at a certain grain size, and that the expansion decreased when the size was increased or decreased from that pessimum size [17].

Vivian showed that alkali-reactive opal aggregate had a pessimum proportion in the range of 5–10% [18]. Based on the assumption that the expansion of concrete was induced by the formation of hydrated alkali silicate, he explained the effect as due to two counteracting effects on the expansion of alkali silicate. Increase of the proportion increased the total volume of expansive alkali silicate, so that the expansion initially increased with increasing proportion. Too much increase of the proportion, however, significantly decreased the concentration of alkali in the alkali silicate, which decreased the expansion of the alkali silicate. The expansion therefore became the maximum at a pessimum proportion and then decreased. Another possible explanation is that the increase of reactive aggregate causes rapid consumption of alkali hydroxide to form alkali silicate near the surface of the aggregate. The alkali silicate near the surface is highly hydrated to give fluid alkali silicate, which does not give any expansive pressure.

These explanations are based on the assumption that the amount of alkali hydroxide is limited. The pessimum effect would not be expected if the expansion of concrete is measured in an accelerated mortar bar test in which the concrete is stored in a 1 $mol/dm^3$ NaOH solution at 80 °C, since alkali hydroxide is continuously supplied from the outside into the concrete. However, the pessimum proportion was also observed in the accelerated mortar bar test. Bleszynski and Thomas observed the expansion of concrete containing reactive flint sand and inert limestone under the accelerated test condition for two to three years, and found that the expansion was the maximum at the proportion of 25% flint [10]. They observed distinct reaction rims around the ASR-affected aggregate particles. Concrete with 100% flint scarcely expanded and showed no reaction rims around the aggregate suffered from alkali–silica reaction. They also found that the addition of 90 $kg/m^3$ of $Ca(OH)_2$ at the time of concrete preparation significantly increased the expansion, especially for the concrete with 100% flint. Bektas et al. also obtained the similar results by using chert as a reactive aggregate [19]. Although Shayan attributed the decrease of the expansion at higher proportion as due to the formation of a barrier to the penetration of the NaOH solution, which was generated by the penetrated NaOH and reactive aggregate in the outer skin of the concrete [20], such a barrier was not observed in their samples. The pessimum proportion effect was thus observed even though the supply of alkali hydroxide was unlimited.

The pessimum size effect has been explained in much the same manner as the pessimum proportion effect. The decrease of concrete expansion with decreasing size of aggregates is generally considered as due to the easier release of the expansive pressure by the penetration of expansive alkali silicate to the surroundings. Although numerous investigations have been carried out on the pessimum size effect [21–32], since the experimental conditions were different with each other, it is difficult to generalize the pessimum size. Many researchers obtained significant and insignificant expansions at the sizes of 0.5 to 2 mm and less than 50 to 150 μm [24–27,29–31], respectively, whereas some researchers obtained insignificant expansion for aggregates much smaller than 50 μm [21,23,28].

Although several models have been proposed so far for explaining the pessimum effects, because of the lack of a definite ASR model, none of them are satisfactory. In the present paper, the pessimum proportion and size effects will be explained based on our ASR model. It will be shown that using very reactive siliceous minerals under anti-pessimum conditions is very effective not only for inhibiting the ASR but also for improving the strength and durability of concrete structures.

## 2. Proposed mechanisms and discussion

### 2.1. ASR model

Explanation of the pessimum effects according to our model necessitates a slight improvement of the model by taking the difference of alkali silicates on and beneath the surface of aggregate into consideration. The previous experimental study on the reactions of glass beads with alkaline and $Ca(OH)_2$ solutions gave the following results [14,15];

1) Immersion of a viscous $Na_2Si_2O_5(H_2O)_{8.4}$ water glass droplet into a saturated aqueous solution of $Ca(OH)_2$ caused the dissolution of the droplet. The dissolved water glass then converted to fragmental calcium alkali silicate. Immersion of a water glass bead, prepared by drying a water glass droplet, into the solution generated a white layer of calcium alkali silicate around the beads, which was then broken by inner water glass that was swollen by absorbing water through the semi-permeable silicate layer. These results indicated that the tight and strong layer of calcium alkali silicate was not generated from mature alkali silicate. The formation of a tight and strong reaction rim necessitates the presence of immature alkali silicate containing less water and less alkali ions.
2) As summarized in Table 1, three of five hard glass beads (5 mm in diameter, a model material of reactive aggregate) were cracked by immersing in aqueous solutions at 80 °C only in the order of 0.1 N NaOH, saturated $Ca(OH)_2$ and then 0.1 N NaOH. This indicates that a reaction rim with enough strength for accumulating the expansive pressure for cracking the bead is generated by the reaction of $Ca^{2+}$ ions with a preexisting immature alkali silicate layer surrounding the bead, and the NaOH solution can penetrate through the reaction rim [33–35] into the glass bead to generate an expansive pressure by producing new hydrated alkali silicate. The formation of a small amount of fragmental calcium alkali silicate around the glass beads was observed immediately after the immersion of the NaOH-immersed glass beads in the $Ca(OH)_2$ solution. The outermost layer of the glass bead was therefore composed of mature alkali silicate, and immature alkali silicate layer below the mature layer was converted to the reaction rim.

Fig. 1 shows the schematic representation of the proposed ASR model with emphasis on the role of mature and immature alkali silicates. For making the model simpler, the central aggregate particle is assumed to be composed of a homogeneous reactive mineral. In case that the particle has a heterogeneous structure with reactive mineral veinlets surrounded by inert minerals, the reaction rim does not necessarily surround the entire particle but at least covers the outlets of the veinlets. The first step of ASR is the scission of three

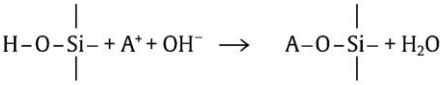
**Table 1**
Effect of chemical treatments on the cracking of hard glass bead [15].

| First treatment | $Ca(OH)_2$ 5 days | NaOH 5 days | NaOH + $Ca(OH)_2$[a] 5 days | $Ca(OH)_2$ 5 days | NaOH 2 days | NaOH 2 days |
|---|---|---|---|---|---|---|
| Second treatment | | | | NaOH 5 days | $Ca(OH)_2$ 5 days | $Ca(OH)_2$ 3 days |
| Third treatment | | | | | Water 3 days | NaOH 1 day |
| Number of cracked beads[b] | 0/5 | 0/5 | 0/5 | 0/5 | 0/5 | 3/5 |

[a] 10:1 mixture of the NaOH and the $Ca(OH)_2$ solutions.
[b] Number of cracked beads within five tested beads.

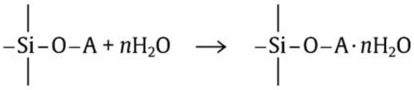
dimensional siloxane networks in aggregate particles by alkali hydroxide AOH to generate alkali silicate.

$$-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + A^+ + OH^- \longrightarrow -\overset{|}{\underset{|}{Si}}-O-A + H-O-\overset{|}{\underset{|}{Si}}-$$



$$H-O-\overset{|}{\underset{|}{Si}}- + A^+ + OH^- \longrightarrow A-O-\overset{|}{\underset{|}{Si}}- + H_2O$$

The resultant oligomeric alkali silicate is highly hygroscopic except for lithium silicate, so that it immediately reacts with nearby water to generate hydrated alkali silicate gel

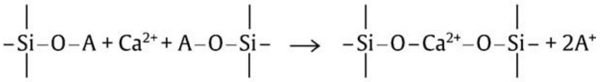


$$-\overset{|}{\underset{|}{Si}}-O-A + nH_2O \longrightarrow -\overset{|}{\underset{|}{Si}}-O-A\cdot nH_2O$$

where $n$ denotes the hydration number. Since the reaction proceeds toward the center of the particle, the concentration of alkali ions and the degree of hydration decreases toward the center. Highly hydrated mature alkali silicate is generated near the surface of the particle, and a part of it is extruded and dissolved into the pore solution. Less hydrated immature solid alkali silicate remains beneath the mature alkali silicate.

The consumption of $OH^-$ ions induces the gradual dissolution of $Ca^{2+}$ ions from $Ca(OH)_2$ into the pore solution, since the maximum concentration of $Ca^{2+}$ ions is inversely proportional to the square of the concentration of $OH^-$ ions, as $[Ca^{2+}] = 0.0000483/[OH^-]^2$ at 25 °C, where $[Ca^{2+}]$ and $[OH^-]$ are the concentrations of $Ca^{2+}$ and $OH^-$ ions in mol/kg.

The mature hydrated alkali silicate on the surface and in the pore solution readily reacts with $Ca^{2+}$ ions, as



$$-\overset{|}{\underset{|}{Si}}-O-A + Ca^{2+} + A-O-\overset{|}{\underset{|}{Si}}- \longrightarrow -\overset{|}{\underset{|}{Si}}-O-Ca^{2+}-O-\overset{|}{\underset{|}{Si}}- + 2A^+$$

to form fragmental calcium alkali silicate, because the reaction accompanies significant reduction of the volume. The immature alkali silicate beneath the surface slowly reacts with $Ca^{2+}$ ions to form a hard and tight reaction rim composed of calcium alkali silicate. The reactive aggregate particle is now tightly packed with the reaction rim. The released alkali hydroxide further reacts with aggregate.

The reaction rim allows the penetration of alkaline solution into the particle but not the extrusion of viscous hydrated alkali silicate from the particle. The alkali silicate newly formed in the particle is therefore accumulated inside of the reaction rim, and is finally released by cracking the reaction rim and the surrounding concrete. Accumulation of the enough amount of alkali silicate necessitates the formation of reaction rim that is thick and tight enough for preventing the penetration of alkali silicate with highly expansive pressure. Due to the inhomogeneity of aggregate particles and their environments, the minimum thickness for keeping the enough amount of alkali silicate may not be uniquely determined but is scattered around some averaged thickness $h_a$. Assuming a normal distribution of the minimum thickness, the probability $p_r$ that a particle with the reaction

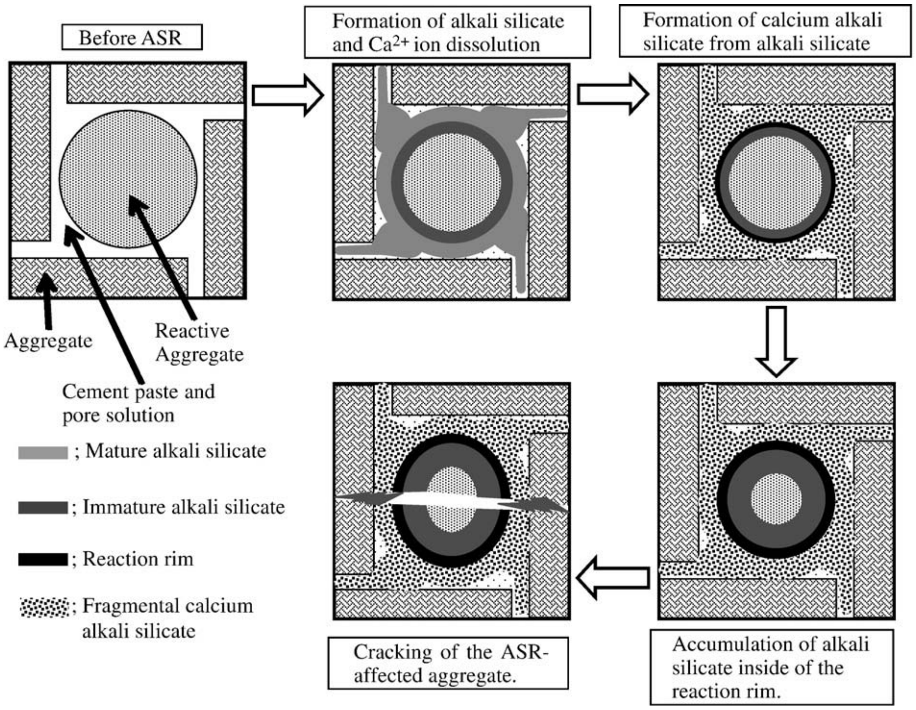


**Fig. 1.** Schematic representation of the mechanism of ASR in concrete.

rim of the thickness $h_r$ can tolerate the accumulation of the alkali silicate is approximately given by

$$p_r = 1 - \frac{1}{\sqrt{2\pi\sigma_r^2}}\int_{h_r}^{\infty} \exp\left[-\frac{1}{2}\left(\frac{h-h_a}{\sigma_r}\right)^2\right]dh$$
$$\approx\begin{cases} 0 & \text{for} \quad h_r \le h_a - 1.5\sigma_r \\ 0.5 + \dfrac{h_r - h_a}{3\sigma_r} & \text{for} \quad h_a - 1.5\sigma_r \le h_r \le h_a + 1.5\sigma_r \\ 1 & \text{for} \quad h_r \ge h_a + 1.5\sigma_r \end{cases} \tag{1}$$

where $\sigma_r$ is the standard deviation for the thickness.

Since a significant amount of $Ca^{2+}$ ions around the particle are consumed by the formation of the fragmental calcium alkali silicate and the reaction rim, the alkali silicate in the aggregate absorbs only a small amount of $Ca^{2+}$ ions even after cracking of the particles. Thomas [36] reported that gels in aggregate in ASR-affected field concrete showed lower Ca/Si atomic ratios of ~0.25, whereas gels in the paste of the same concrete showed much higher Ca/Si atomic ratios of up to 1.3. The former gels correspond to calcium alkali silicate generated inside of the reaction rim, and the latter gels correspond to fragmental calcium alkali silicate generated from the mature and fluid alkali silicate.

The maximum expansive pressure generated by the accumulation of alkali hydroxide is estimated from the relation of $P = \Delta G/V$ [15], where $-\Delta G$ is the free energy released by the formation of alkali silicate with volume $V$. Rough estimation of the pressure gives $P \approx 4 \times 10^8$ Pa, which is two orders of magnitude higher than that for cracking concrete [37]. It should be noted that the expansive pressure arises neither from the osmotic pressure nor from the double layer force. These forces are negligibly weak for cracking concrete [15]. The pressure cracking the concrete is a chemical pressure which originates from the formation of new chemical bonds accompanying the volume expansion of the reaction product.

The aggregate particle generally contains non-reacting and non-reactive minerals. The expansive pressure $P$ under the presence of alkali silicate and the remaining minerals is estimated from the compressibilities of the alkali silicate and the aggregate. Suppose the aggregate particle with volume $U_S$ reacts with alkali hydroxide to convert a reactive mineral of volume $U_A$ to alkali silicate, under the condition that the total volume of the particle is unchanged, the volumes of the compressed alkali silicate, $U$, and the remaining aggregate, $U_S - U$, are given by

$$U \approx \varepsilon U_A \exp(-\kappa_A P) \tag{2}$$

$$U_S - U \approx (U_S - U_A)\exp(-\kappa_S P) \tag{3}$$

where $\varepsilon$ is the reaction-induced volume expansion ratio of the reactive mineral at the atmospheric pressure, and $\kappa_S$ and $\kappa_A$ are the compressibilities of the aggregate and the resultant alkali silicate, respectively. Since the values of $\kappa$ for condensed materials are of the order of $10^{-10}$ to $10^{-11}$ $Pa^{-1}$ and $P$ is less than $10^7$ Pa, the conditions of $\kappa P \ll 1$ and therefore $\exp(-\kappa P) \approx 1 - \kappa P$ are generally fulfilled. Then, substitution of Eq. (2) into Eq. (3) gives the relation between $U_A$ and $P$ as

$$\frac{U_A}{U_S} \approx \frac{\kappa_S P}{\varepsilon - 1 - \varepsilon\kappa_A P + \kappa_S P} \approx \frac{\kappa_S P}{\varepsilon - 1} \equiv \alpha P \tag{4}$$

The above relation indicates that the remaining minerals are compressed by the surrounding expansive alkali silicate to reduce the expansive pressure.

The aggregate particles are cracked once the expansive pressure estimated from Eq. (4) exceeds the tolerance of the reaction rims and the surrounding concrete. Since the aggregate particles and their environments are inhomogeneous, the minimum pressure for cracking the particles and the surrounding concrete may not be uniquely determined but is scattered around some averaged pressure $P_a$. Assuming a normal distribution of the minimum pressure, the probability $p_c$ that alkali silicate cracks the particle is given by

$$p_c = 1 - \frac{1}{\sqrt{2\pi\sigma_c^2}}\int_{U_A/\alpha U_S}^{\infty} \exp\left[-\frac{1}{2}\left(\frac{P-P_a}{\sigma_c}\right)^2\right]dP$$
$$\approx\begin{cases} 0 & \text{for} \quad U_A \le (P_a - 1.5\sigma_c)\alpha U_S \\ 0.5 + \dfrac{U_A - \alpha U_S P_a}{3\sigma_c \alpha U_S} & \text{for} \quad (P_a - 1.5\sigma_a)\alpha U_S \le U_A \\ & \qquad \le (P_a + 1.5\sigma_c)\alpha U_S \\ 1 & \text{for} \quad U_A \ge (P_a + 1.5\sigma_c)\alpha U_S \end{cases} \tag{5}$$

where $\sigma_c$ is the standard deviation for the critical pressure.

### 2.2. Pessimum effects

The relation between the expansion and the proportion and the size of reactive aggregate can be estimated semi-quantitatively by using the ASR model shown in Fig. 1. Suppose concrete initially contains $[AOH]_0$ of reactive alkali hydroxide, $[Ca(OH)_2]_0$ of reactive $Ca(OH)_2$, where [ ] denotes molar concentration, and the number density $N$ of reactive aggregate particles with constant radius $r$. The alkali hydroxide converts the surface layers of the aggregate particles to mature alkali silicate. Defining $h_m$ as the thickness of the layers converted to the mature alkali silicate, the amount of remaining alkali hydroxide usable for generating alkali silicate inside of the reaction rims is given by

$$[AOH] = [AOH]_0 - \frac{4\pi a' h_m\left(3r^2 - 3rh_m + h_m^2\right)}{3}N \tag{6}$$

where $a'$ is the net amount of consumed alkali hydroxide per unit volume of the aggregate. The net amount is much smaller than the amount of alkali hydroxide necessary for the formation of the alkali silicate, $a$, because a significant part of the reacted alkali hydroxide is recovered afterward by the reaction with $Ca^{2+}$ ions [9,36,38]. The maximum amount of aggregate minerals in each particle that is consumable by the remaining alkali hydroxide is given by

$$U_A = \frac{[AOH]}{aN} = \frac{[AOH]_0}{aN} - \frac{4\pi a' h_m\left(3r^2 - 3rh_m + h_m^2\right)}{3a}. \tag{7}$$

A part of $Ca^{2+}$ ions are consumed by the mature alkali silicate to form fragmental calcium alkali silicate. The amount of remaining $Ca(OH)_2$ usable for the formation of reaction rims is given by

$$[Ca(OH)_2] = [Ca(OH)_2]_0 - \frac{4\pi b h_m\left(3r^2 - 3rh_m + h_m^2\right)}{3}N \tag{8}$$

where $b$ is the amount of consumed $Ca^{2+}$ ions per unit volume of the aggregate particles. The outer layers of the particles are removed by the formation of fragmental calcium alkali silicate, so that the radius of the particles is now reduced to $r - h_m$. Tiny aggregate particles with $r < h_m$ are therefore impossible to generate expansive pressure by alkali–silica reaction. The total remaining volume of the particles that can be consumed for generating the expansive pressure is given by

$$V = \frac{4\pi(r - h_m)^3}{3}N. \tag{9}$$

The remaining $Ca(OH)_2$ is possible to generate reaction rims with the thickness $h_r$ that satisfies the relation of

$$\frac{4\pi b}{3}\left[3(r-h_m)^2 h_r - 3(r-h_m)h_r^2 + h_r^3\right]N = \left[Ca(OH)_2\right]. \tag{10}$$

The degree of expansion by the cracking of particles, $E_X$, is proportional to the total volume of the cracking particles, so that

$$E_X = \frac{4\pi(r-h_m)^3}{3} e p_r p_c N \tag{11}$$

where $e$ is the expansion coefficient. The relation between the degree of expansion and the proportion and the size of reactive aggregate will be discussed in the following section.

### *2.2.1. Pessimum proportion effect*

According to the ASR model mentioned above, the pessimum proportion effect can be explained as follows;

Suppose alkali hydroxide is continuously supplied from the outside into concrete. Increase of the proportion of reactive aggregate initially increases the ASR expansion due to the increase of the amount of aggregate particles that are cracked by the formation of alkali silicate. Increase of the proportion increases the amount of mature alkali silicate. The formation of reaction rims then becomes difficult, because most of $Ca(OH)_2$ in concrete is consumed by the reaction with mature alkali silicate to form fragmental calcium alkali silicate. The expansion thereby reduces after passing a pessimum proportion. Addition of extra $Ca(OH)_2$ in concrete helps the formation of the reaction rims so that the pessimum proportion increases.

Suppose the amount of alkali hydroxide in concrete is limited. Increase of the proportion increases the amount of aggregate particles with alkali silicate enough for cracking the particles, so that the expansion of concrete initially increases with increasing proportion. Increase of the proportion, however, decreases the amount of alkali hydroxide per particle, which reduces the amount of alkali silicate in each particle and thereby prevents the cracking of the particles. The expansion thereby reduces after passing a pessimum proportion.

It should be noted that the pessimum proportion effect is defined under the condition that the expansion of concrete due to ASR is terminated. Because the rate of ASR increases with the proportion, the degree of ASR-induced expansion may monotonically increase with the proportion at the initial stage of ASR expansion.

The relation between the pessimum proportion and the contents of alkali hydroxide and $Ca(OH)_2$ is given in the following section. Unless otherwise stated, alkali hydroxide and $Ca(OH)_2$ in concrete are assumed to react solely with ASR-inducing aggregate. If co-existing ASR-tolerant aggregate competes the consumption of alkali hydroxide and $Ca(OH)_2$ with ASR-inducing aggregate, because the consumption by the ASR-tolerant aggregate decreases with increasing proportion of the ASR-inducing aggregate, the expansion is possible to increase monotonically with the proportion of the ASR-inducing aggregate. For simplicity's sake, the relations of $r \gg h_m$, $r \gg h_r$ and $a' \ll a$ are assumed in the mathematical treatment.

**Case 1.** The amount of $Ca(OH)_2$ is limited but the amount of alkali hydroxide is limitless.

When alkali hydroxide is continuously supplied from the outside, like the accelerated mortar bar test, the amount of remaining $Ca(OH)_2$ usable for the formation of reaction rim determines the expansion. Eq. (1) gives the relation between the number of aggregate particles and the probability of forming reaction rims with enough strength. Under the condition that the number of aggregate particles is small enough for the remaining $Ca(OH)_2$ to generate strong reaction rims on all the particles, or

$$h_r = \frac{\left[Ca(OH)_2\right]_0 - 4\pi r^2 h_m b N}{4\pi r^2 b N} \geq h_a + 1.5\sigma_r, \tag{12}$$

$$\therefore \quad N \leq \frac{\left[Ca(OH)_2\right]_0}{4\pi r^2 b(h_a + h_m + 1.5\sigma_r)}$$

the degree of expansion is determined by the total volume of the aggregate and is given by

$$E_X = \frac{4\pi r^3}{3} e N \tag{13}$$

The degree of expansion thus initially increases with increasing proportion.

Increase of the proportion causes the deficiency of $Ca(OH)_2$ usable for the formation of strong reaction rims. Under the condition of

$$\frac{\left[Ca(OH)_2\right]_0}{4\pi r^2 b(h_a + h_m + 1.5\sigma_r)} \leq N \leq \frac{\left[Ca(OH)_2\right]_0}{4\pi r^2 b(h_a + h_m - 1.5\sigma_r)} \tag{14}$$

only a part of the particles can prepare reaction rims that are thick enough for confining alkali silicate. The degree of expansion is then given by

$$E_X = \frac{4\pi r^3}{3} e p_r N = \frac{er}{9\sigma_r b}\left[\left[Ca(OH)_2\right]_0 - 4\pi r^2 b(h_a + h_m - 1.5\sigma_r)N\right] \tag{15}$$

The degree of expansion thus decreases after passing a pessimum proportion.

The expansions given by Eqs. (13) and (15) are the same at the pessimum proportion $N_p$, so that

$$N_p = \frac{\left[Ca(OH)_2\right]_0}{4\pi r^2 b(h_a + h_m + 1.5\sigma_r)} \tag{16}$$

The pessimum proportion increases with the initial amount of calcium hydroxide, which agrees with experimental evidence [10].

**Case 2.** Both the amounts of alkali hydroxide and $Ca(OH)_2$ are limited.

This is the most realistic case for field concrete. When all the aggregate particles prepare the strong rims and the amount of alkali hydroxide is enough for all the particles to produce alkali silicate enough for cracking, or

$$N \leq \frac{\left[Ca(OH)_2\right]_0}{4\pi r^2 b(h_a + h_m + 1.5\sigma_r)} \quad \text{and} \quad N \leq \frac{3[AOH]_0}{4\pi r^3 \alpha a(P_a + 1.5\sigma_c)} \tag{17}$$

the degree of expansion is expressed by Eq. (13).

Increase of the proportion increases the amounts of alkali hydroxide and $Ca(OH)_2$ that are required for cracking the particles. When only the amount of remaining alkali hydroxide is enough for cracking all the particles, the degree of expansion and the pessimum proportion are given by Eqs. (15) and (16), respectively. When the amount of the remaining alkali hydroxide is not enough for generating enough amount of alkali silicate in all the aggregate particles, or

$$\frac{3[AOH]_0}{4\pi r^3 \alpha a(P_a + 1.5\sigma_c)} \leq N \leq \frac{3[AOH]_0}{4\pi r^3 \alpha a(P_a - 1.5\sigma_c)} \tag{18}$$

but the amount of remaining $Ca(OH)_2$ is enough for generating reaction rims on all the particles, the degree of expansion is given by

$$E_X = \frac{4\pi r^3}{3} e p_c N = \frac{e}{3\sigma_c}\left[\frac{[AOH]_0}{\alpha a} - \frac{4\pi r^3(P_a - 1.5\sigma_c)}{3}N\right] \tag{19}$$

The degree of expansion thus decreases after passing the pessimum proportion that is derived from Eqs. (13) and (19) as

$$N_p = \frac{3[\mathrm{AOH}]_0}{4\pi r^3 (P_a + 1.5\sigma_c)\alpha a} \tag{20}$$

The pessimum proportion increases with the initial concentration of alkali hydroxide, which accords with experimental evidence [18].

When the amount of remaining $Ca(OH)_2$ is also insufficient, or

$$\frac{[\mathrm{Ca}(OH)_2]_0}{4\pi r^2 b(h_a + h_m + 1.5\sigma_r)} \le N \le \frac{[\mathrm{Ca}(OH)_2]_0}{4\pi r^2 b(h_a + h_m - 1.5\sigma_r)} \tag{14}$$

The degree of expansion is given by

$$E_X = \frac{4\pi r^3}{3} e p_r p_c N = \frac{e}{36\pi r^2 b \sigma_r \sigma_c N}\left[\frac{[\mathrm{AOH}]_0}{\alpha a} - \frac{4\pi r^3 (P_a - 1.5\sigma_c)N}{3}\right] \times \left[[\mathrm{Ca(OH)_2}]_0 - 4\pi r^2 b(h_a + h_m - 1.5\sigma_r)N\right] \tag{21}$$

The degree of expansion decreases more significantly by the deficiency of both alkali hydroxide and $Ca(OH)_2$. The pessimum proportion is given either by Eq. (16) or by Eq. (20).

Using a standard concrete prism test in which a concrete sample was stored at 38 °C and 100% relative humidity for more than one year, Nixon et al. measured the expansion of concrete containing flint as a reactive aggregate and 0.96% $Na_2O$ equivalent by mass of cement, and found the pessimum proportion of 10% [38]. The pessimum proportion they obtained is not much different from the pessimum proportion of 25% that was obtained under the accelerated mortar bar test by immersing the concrete with flint aggregate in 1 M NaOH solution [10]. Using Eqs. (16) and (20), the ratio of the pessimum proportions between the prism (alkali hydroxide-limited) and the mortar bar ($Ca(OH)_2$-limited) tests is given by

$$N_p([\mathrm{Ca(OH)_2}]_0) : N_p([\mathrm{AOH}]_0) = \frac{[\mathrm{Ca(OH)_2}]_0}{4\pi r^2 b(h_a + h_m + 1.5\sigma_r)} : \frac{3[\mathrm{AOH}]_0}{4\pi r^3 (P_a + 1.5\sigma_c)\alpha a} \tag{22}$$

Here the values of parameters are roughly $[Ca(OH)_2]_0/[AOH]_0 \approx 10$, $a \approx 2b$, $r \approx 10^{-3}$ m, $(P_a + 1.5\sigma_c)\alpha \approx 10^{-3}$, and $N_p([Ca(OH)_2]_0)$: $N_p([AOH]_0) = 2.5$:1. Substitution of these values into Eq. (22) gives $(h_a + h_m + 1.5\sigma_r) = 10^{-6}$–$10^{-5}$ m, which suggests that the radius of more than a few µm is necessary for accumulating the expansive pressure in the aggregate particles.

### 2.2.2. Pessimum size effect

As shown in the previous section, the degree of expansion depends both on the number and the size of aggregate particles. Reactive aggregate particles do not cause the ASR of concrete unless $r > h_m$, because otherwise the particles are entirely consumed for the formation of fragmental calcium alkali silicate. The degree of expansion therefore initially increases with increasing particle size.

For removing the complexity of mathematical expressions, the relations of $r > h_m + h_r$ and $a' \gg a'$ will be assumed in the following treatments. The pessimum size effect has been observed by fixing the proportion of reactive aggregate, so that the variable $N$ is changed to $N = 3\ V_0/(4\pi r^3)$, where $V_0$ is the total volume of the reactive aggregate. Eqs. (7)–(11) are then rewritten as

$$U_A = \frac{4\pi r^3 [\mathrm{AOH}]_0}{3aV_0} \tag{7'}$$

$$[\mathrm{Ca(OH)_2}] = [\mathrm{Ca(OH)_2}]_0 - \frac{3bh_m V_0}{r} \tag{8'}$$

$$V = V_0 \tag{9'}$$

$$h_r = \frac{[\mathrm{Ca(OH)_2}]_0}{3bV_0} r - h_m \tag{10'}$$

$$E_X = eV_0 p_r p_c \tag{11'}$$

Substitution of Eq. (7′) into Eq. (5) gives

$$p_c \approx \begin{cases} 0 & \text{for } [AOH]_0/(aV_0) \le (P_a - 1.5\sigma_c)\alpha \\ 0.5 + \dfrac{[AOH]_0/(aV_0) - \alpha P_a}{3\sigma_c \alpha} & \text{for } (P_a - 1.5\sigma_a)\alpha \le [AOH]_0/(aV_0) \le (P_a + 1.5\sigma_c)\alpha \\ 1 & \text{for } [AOH]_0/(aV_0) \ge (P_a + 1.5\sigma_c)\alpha \end{cases} \tag{23}$$

which implies that the probability of cracking after the formation of strong reaction rims does not depend on the radius of the aggregate particles. The degree of expansion solely depends on $p_r$. We will assume in the following treatment that $[AOH]_0/(aV_0) \ge (P_a + 1.5\sigma_c)\alpha$, or the amount of alkali hydroxide is enough for cracking all the aggregate particles. Since the necessary amount of alkali hydroxide does not depend on the particle radius, this assumption does not influence the general conclusion of the pessimum size effect obtainable from the following treatment.

Substitution of Eq. (10′) into Eq. (1) gives the probability of generating the reaction rim thick enough for accumulating the expansive pressure for cracking, as

$$p_r \approx \begin{cases} 0 & \text{for } r \le \dfrac{3bV_0(h_a + h_m - 1.5\sigma_r)}{[Ca(OH)_2]_0} \\ 0.5 + \dfrac{[Ca(OH)_2]_0 r - 3bV_0(h_a + h_m)}{9b\sigma_r V_0} & \text{for } \dfrac{3bV_0(h_a + h_m - 1.5\sigma_r)}{[Ca(OH)_2]_0} \le r \le \dfrac{3bV_0(h_a + h_m + 1.5\sigma_r)}{[Ca(OH)_2]_0} \\ 1 & \text{for } r \ge \dfrac{3bV_0(h_a + h_m + 1.5\sigma_r)}{[Ca(OH)_2]_0} \end{cases} \tag{24}$$

The value of $p_r$ increases with increasing $r$, because the increase of the particle radius reduces the amount of mature alkali silicate which then absorbs calcium ions to prevent the formation of strong reaction rim. Since $p_c$ is constant and $p_r$ increases with $r$, the degree of expansion monotonically increases with increasing particle size of the reactive aggregate. The pessimum size effect is therefore impossible to be derived from the treatment of the ASR so far mentioned.

The decrease of the expansion after passing the pessimum size can be explained by taking the rate of chemical reaction into account. As will be mentioned in detail in the following section, increase of the aggregate size lowers the rate of ASR. Therefore, if alkali hydroxide and $Ca(OH)_2$ in concrete are consumed both by ASR-inducing and co-existing ASR-tolerant aggregates, increase of the size of the ASR-inducing aggregate decrease the amount of the alkali hydroxide and $Ca(OH)_2$ consumed by the aggregate. The ASR-induced expansion thereby decreases after passing a pessimum size. Alternatively, if the expansion is measured before the termination of the expansion, the pessimum size is observable even if the alkali hydroxide and $Ca(OH)_2$ are not consumed by ASR-tolerant aggregate. The rate of ASR is highly dependent on the size of aggregate particles, so that larger particles are scarcely cracked while the ASR of smaller particles is terminated.

The pessimum size effect arising from the former mechanism is easily understandable by replacing constants $[AOH]_0$ and $[Ca(OH)_2]_0$ in Eqs. (23) and (24), respectively, with functions that monotonically decrease with increasing particle size. We therefore treat the latter case in detail.

The reaction between alkali hydroxide and siliceous minerals in aggregate is described by a diffusion equation with a chemical reaction between alkali hydroxide and the aggregate, as

$$\frac{\partial A(\mathbf{r},t)}{\partial t} = \nabla D(S(r,t)) \cdot \nabla A(\mathbf{r},t) - kS(\mathbf{r},t)A(\mathbf{r},t) \tag{25}$$

$$\frac{\partial S(\mathbf{r},t)}{\partial t} = -kS(\mathbf{r},t)A(\mathbf{r},t) \tag{26}$$

where $A(\mathbf{r},t)$ and $S(\mathbf{r},t)$ are the concentration of alkali hydroxide and reactive siliceous minerals in the aggregate, respectively, $D(S(\mathbf{r},t))$ is the diffusion coefficient of alkali hydroxide in the aggregate, and $k$ is the rate constant of alkali–silica reaction.

Assuming that the depth of alkali silicate layer is much shorter than the radius of the aggregate and the diffusion coefficient does not depend on the concentration of alkali silicate in the aggregate, the above equations are simplified to,

$$\frac{\partial A(x,t)}{\partial t} = D\frac{\partial^2 A(x,t)}{\partial x^2} - kS(x,t)A(x,t) \tag{27}$$

$$\frac{\partial S(x,t)}{\partial t} = -kS(x,t)A(x,t). \tag{28}$$

The initial and the boundary conditions of the above equations are

$$A(x>0,0) = 0, \quad S(x,0) = S_0, \quad A(0,t) = A_0 \tag{29}$$

The value of $A_0$ might be proportional to the concentration of alkali hydroxide in the pore solution.

Defining

$$p = \sqrt{kS_0/D}x, \quad q = kS_0t, \quad c = \frac{A_0}{S_0}, \quad F(p,q) = \frac{A(x,t)}{S_0}, \quad G(p,q) = \frac{S(x,t)}{S_0}. \tag{30}$$

Eqs. (27)–(29) are rewritten as

$$\frac{\partial F(p,q)}{\partial q} = \frac{\partial^2 F(p,q)}{\partial p^2} - F(p,q)G(p,q) \tag{31}$$

$$\frac{\partial G(p,q)}{G(p,q)\partial q} = -F(p,q) \tag{32}$$

$$F(p>0,0) = 0, \quad G(p,0) = 1 \quad F(0,q) = c. \tag{33}$$

Substitution of Eq. (32) into Eq. (31) leads to

$$\frac{\partial}{\partial q}\left(\frac{\partial \ln G(p,q)}{\partial q}\right) = \frac{\partial}{\partial q}\left(\frac{\partial^2 \ln G(p,q)}{\partial p^2} - G(p,q)\right). \tag{34}$$

Integration of Eq. (32) at $p=0$ gives a boundary condition for $G(p,q)$ as

$$\ln G(0,q) = -cq. \tag{35}$$

Integration of Eq. (34) leads to

$$\frac{\partial \ln G(p,q)}{\partial q} = \frac{\partial^2 \ln G(p,q)}{\partial p^2} - G(p,q) + f(p). \tag{36}$$

The constant of integration, $f(p)$, is determined from the initial condition of

$$\left[\frac{\partial \ln G(p,q)}{\partial q}\right]_{q=0} = 0, \quad \frac{\partial^2 \ln G(p,0)}{\partial p^2} = 0, \quad G(p,0) = 1$$

as $f(p)=1$. Eq. (36) is therefore written as

$$\frac{\partial \ln G(p,q)}{\partial q} = \frac{\partial^2 \ln G(p,q)}{\partial p^2} - G(p,q) + 1. \tag{37}$$

Although the analytical solution of Eq. (37) is difficult to be obtained, the numerical solution is easily obtained by using the initial and boundary conditions given by Eqs. (33) and (35). Fig. 2 shows the spatial distribution of the concentration of siliceous minerals as a function of reaction time. Defining reaction depth $H(t)$ as a position where the relation of $\ln G[H(t), q] = -1$ is satisfied, as shown in Fig. 3, this is linearly dependent on the square root of the reaction time, as

$$H(t) \approx \sqrt{1.88A_0Dt/S_0} \tag{38}$$

Increase of the reaction depth of two times therefore needs the reaction time of four times.

The amount of alkali silicate in the aggregate particle at time $t$ is approximately given by

$$U_A = \frac{4\pi r^3 - 4\pi[r - H(t)]^3}{3} \tag{39}$$

Substitution of Eq. (39) into Eq. (5) leads

$$p_c \approx \begin{cases} 1 & \text{for} \quad r \le H(t)/\left[1 - (1 - P_a\alpha - 1.5\sigma_c\alpha)^{1/3}\right] \\ \dfrac{1 - P_a\alpha + 1.5\sigma_c\alpha - [1 - H(t)/r]^3}{3\sigma_c\alpha} & \text{for} \quad H(t)/\left[1 - (1 - P_a\alpha - 1.5\sigma_c\alpha)^{1/3}\right] \le r \\ & \quad \le H(t)/\left[1 - (1 - P_a\alpha + 1.5\sigma_c\alpha)^{1/3}\right] \\ 0 & \text{for} \quad r \ge H(t)/\left[1 - (1 - P_a\alpha + 1.5\sigma_c\alpha)^{1/3}\right] \end{cases} \tag{40}$$

Eq. (40) indicates that the expansion starts after the induction time of $t = S_0\{1 - [1 - (P_a - 1.5\sigma_c)\alpha]^{1/3}\}^2 r^2/(1.88A_0D)$, and terminates at $t = S_0\{1 - [1 - (P_a + 1.5\sigma_c)\alpha]^{1/3}\}^2 r^2/(1.88A_0D)$.

Fig. 4 shows the schematic representation of the relation between ASR expansion and the size of ASR-inducing aggregate. The expansion given by Eq. (11′) ($E_X = eV_0p_rp_c$) is a function of $p_r$ and $p_c$ that are given by Eqs. (24) and (40), respectively. If the amount of $Ca(OH)_2$ is large enough or the amount of ASR-inducing aggregate is small enough to prepare strong rims on all the aggregate particles, since $p_r$

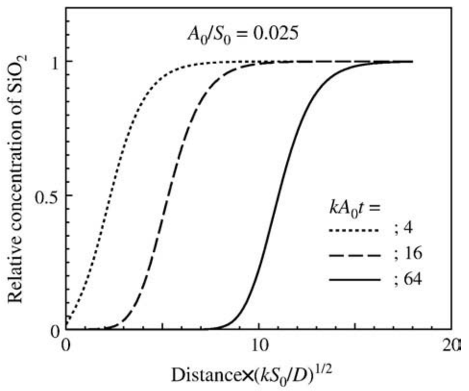


**Fig. 2.** Spatial distribution of siliceous minerals in aggregate as a function of reaction time.

becomes unity, the expansion solely depends on $p_c$. The value of $p_c$ initially increases with increasing $r$, because the value of $V_0$ remaining after the formation of mature alkali silicate increases. The value of $p_c$ then becomes constant until $r$ approaches the reaction depth $H\{t\}$, and then decreases with increasing $r$. The expansion-versus-radius curve is therefore trapezoidal showing no distinct pessimum size (dashed line). Alternatively, if the time of ASR measurement is long enough to complete the ASR for all the aggregates, since $p_c$ becomes unity and $p_r$ increases with increasing $r$, the expansion-versus-radius curve also shows no pessimum size (dotted line).

As shown with a solid line in Fig. 4, the pessimum size effect is observable under the condition that $p_r$ and $p_c$ are neither unity.

$$\frac{3bV_0(h_a + h_m - 1.5\sigma_r)}{[\mathrm{Ca(OH)_2}]_0} \le r \le \frac{3bV_0(h_a + h_m + 1.5\sigma_r)}{[\mathrm{Ca}(OH)_2]_0}$$

and

$$H(t) / \left[1 - (1 - P_a\alpha - 1.5\sigma_c\alpha)^{1/3}\right] \le r \le H(t) / \left[1 - (1 - P_a\alpha + 1.5\sigma_c\alpha)^{1/3}\right] r$$

Under the above conditions, the degree of expansion is given by

$$E_X(r) = p_r p_c e V_0 = \frac{1 - P_a\alpha + 1.5\sigma_c\alpha - [1 - H(t)/r]^3}{3\sigma_c\alpha} \times \frac{[\mathrm{Ca(OH)_2}]_0 r + 3bV_0(1.5\sigma_r - h_a - h_m)}{9b\sigma_r} e \tag{41}$$

The first term in the right side of Eq. (41) increases with increasing $r$, whereas the second term decreases, so that the relation of $\mathrm{d}E_X(r)/\mathrm{d}r = 0$ gives the pessimum size. Using an approximation of $[1 - H(t)/r]^3 \approx 1 - 3H(t)/r$, the pessimum size $r_p$ is given by

$$r_p \approx \left[\frac{9bV_0(h_a + h_m - 1.5\sigma_r)}{\alpha[Ca(OH)_2]_0(P_a - 1.5\sigma_c)} H(t)\right]^{1/2} \tag{42}$$

$$= \left[\frac{9bV_0(h_a + h_m - 1.5\sigma_r)}{\alpha[Ca(OH)_2]_0(P_a - 1.5\sigma_c)}\right]^{1/2} \left(\frac{1.88A_0D}{S_0}\right)^{1/4} t^{1/4}$$

The pessimum size decreases with increasing the amount of $\mathrm{Ca(OH)_2}$ per unit volume of the aggregate, or $[\mathrm{Ca(OH)_2}]_0/V_0$, because the increase compensates the deficiency of $\mathrm{Ca(OH)_2}$ arising from the absorption of $\mathrm{Ca^{2+}}$ ions by mature alkali silicate and helps the formation of strong reaction rims on smaller aggregate particles. The pessimum size increases with increasing the concentration of alkali hydroxide, or $A_0$, because the increase accelerates the formation of alkali silicate and thereby helps the accumulation of an enough amount of alkali silicate for larger aggregate particles.

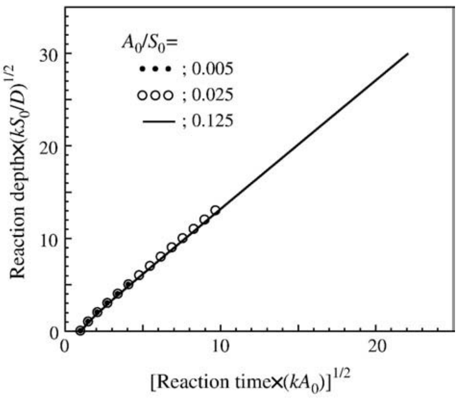


**Fig. 3.** Reaction depth of alkali–silica reaction in aggregate as a function of reaction time.

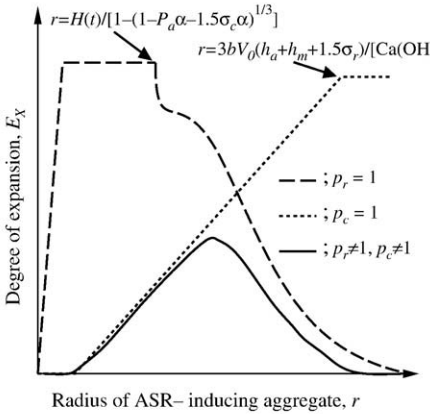


**Fig. 4.** Schematic representation of the relation between ASR expansion and the size of ASR-inducing aggregate under the condition that the ASR of larger aggregate is not completed. The pessimum size effect similar to the solid line is also observable if a significant amount of alkali hydroxide and/or $\mathrm{Ca(OH)_2}$ is consumed by co-existing ASR-tolerant aggregate.

Although the pessimum size thus obtained is a function of time, we usually observe a fixed pessimum size, because the measurement of expansion is terminated within a finite period. Two times increase of the pessimum size needs eight times increase of the time for the measurement.

### 2.3. Pozzolanic effect

Analysis of the pessimum effects indicates that the addition of reactive siliceous minerals with the particle size much smaller than the pessimum size and the amount much larger than the pessimum proportion is possible to suppress ASR. Based on numerous studies on the mitigation of ASR by additives, it has been established that the appropriate use of very fine alkali-reactive siliceous admixtures such as fly ash [39], dispersed silica fume [40,41], municipal waste incinerator bottom ash [42], ground reactive aggregate [43], and ground granulated blast-furnace slag [44–46]. Although the self-consistent mechanism of the ASR mitigation has not been clarified yet, the conclusions are summarized as follows [47];

1) The finer the admixtures is, the better for the mitigation [48].
2) Admixtures with low CaO content act as ASR inhibitors, whereas those with more than 10% CaO content act as ASR promoters.
3) Replacement of approximately 10% or 15–30% of ordinary Portland cement with silica fume or low CaO fly ash, respectively, mitigates ASR.

The above-mentioned mechanism of pessimum effects gives the clear reason why the replacement of the cement with these highly alkali-reactive fine admixtures inhibits the ASR of concrete. The admixtures with low CaO content inhibit the ASR because, due to their large specific surface area, they preferentially reacts with alkali hydroxide to convert to mature alkali silicate which further absorb $\mathrm{Ca(OH)_2}$ in the concrete to prevent the formation of reaction rims around less reactive larger aggregate. The ASR is thereby inhibited. The strength and the durability of the concrete is improved by the admixtures, since mature alkali silicate generated from the admixtures fills the micro pores and is converted there to solid calcium alkali silicate. The admixtures thus act both as ASR inhibitors and pozzolanic materials.

Bleszynski and Thomas examined the ASR expansion of concrete by using the accelerated mortar bar test, and observed no ASR expansion and no reaction rims in concrete containing reactive flint aggregate and 66% fly ash by mass of cement, though the aggregate completely reacted with NaOH coming from the immersing solution

[10]. Their finding supports our conclusion that the admixtures suppress the ASR by absorbing $Ca(OH)_2$.

The function of admixtures as inhibitors for ASR arises from the complete conversion to hydrated mature alkali silicate without leaving reactive siliceous minerals that cause the formation of expansive pressure after the formation of tight reaction rims. The radii of the admixtures must therefore be shorter than $h_m$, the thickness of the surface layer of aggregate changing to mature alkali silicate. Many experimental results on the pozzolanic effect of admixtures suggest that the value of $h_m$ is approximately 25 µm, which accords with our order estimation of $h_m \approx 10^{-6}$–$10^{-5}$ m. Addition of alkali-reactive admixtures with the diameter less than 50 µm is thus expected to suppress ASR even if the concrete contains the pessimum amount of reactive aggregate. The ability of suppressing the ASR increases with decreasing size of the aggregate, which agrees with the experimental result [48]. It should be noted that admixtures must be homogeneously dispersed in concrete. Agglomeration of reactive admixture particles in concrete changes them into hazardous reactive aggregate inducing ASR expansion [49].

The ASR-induced deterioration of concrete can be completely suppressed by removing reactive $Ca(OH)_2$ with mature alkali silicate. Assuming that the mature alkali silicate is generated solely from an admixture and the size of the admixture is small enough to leave no immature alkali silicate after the alkali–silica reaction, the amount of the admixture necessary for suppressing the ASR is estimated from the content of reactive $Ca(OH)_2$ in concrete, the molar ratio of Ca and Si in the resultant fragmental calcium alkali silicate and the content of reactive silica in the admixture, as

$$\frac{S_M m}{60} M = \frac{C_C}{74} + \frac{C_M}{56} M \tag{43}$$

where $M$ is the proportion of the admixture by mass of dry cement, $m = \mathrm{Ca/Si} \approx 1$ is the molar ratio in the fragmental calcium alkali silicate [36], $S_M$ and $C_M$ are the contents of reactive $SiO_2$ and CaO in the admixture by mass, and $C_C$ is the content of reactive $Ca(OH)_2$ in hydrated cement by mass of dry cement. The content of $Ca(OH)_2$ in hydrated ordinary Portland cement is approximately 25% by mass of dry cement. Suppose all the $Ca(OH)_2$ in the hydrated cement are possible to react with alkali silicate and the admixture is solely composed of reactive silica, Eq. (42) gives the proportion of $M = 20\%$ or a 17% replacement of the cement with reactive silica such as silica fume. Suppose fly ash contains 60% of reactive silica and 5% of CaO, Eq. (43) gives the proportion of $M = 37\%$ or the replacement of 27%. The actual amount of the admixtures necessary for suppressing the ASR should be less than these values derived from Eq. (43), since the mature alkali silicate is also formed from reactive aggregate. Eq. (43) thus reasonably reproduces experimental results.

Eq. (43) indicates that the amount of admixtures required for inhibiting ASR depends on the composition of reactive silica and calcium in the admixtures. The required amount increases with decreasing silica content and increasing calcium content, which was reported by many researchers [50–55]. The increase of CaO content in admixtures does not only cause the increase of the required amount but also induces the rapid increase of $Ca^{2+}$ ions in the pore solution. The increase of $Ca^{2+}$ ions accelerates the formation of reaction rims around reactive aggregates, so that the ASR is accelerated. Addition of insufficient amount of CaO-rich admixtures therefore enhances the ASR. Several researchers observed the enhancement of ASR by replacing 10 to 15% of cement with CaO-rich fly ashes [56–59].

## 3. Conclusion

The present investigation shows that our new ASR model allows the self-consistent explanation of the pessimum proportion and size effects of reactive aggregate, and the pozzolanic and the ASR-inhibition effects of fine and reactive siliceous particles such as fly ash and silica fume. The principal mechanism of chemical reactions taking place in concrete is as follows.

(1) The first step of the reactions is the attack of alkali hydroxide in the pore solution to reactive aggregate (or admixtures). Since the reaction proceeds from the outside of the aggregate to the inside, the concentrations of alkali ions and the water of hydration decreases with increasing distance from the surface of the aggregate. The outer layer of the aggregate is converted to bulky mature alkali silicate, and the layer of immature alkali silicate is located beneath the outer layer. A part of the mature alkali silicate is extruded and dissolved into the pore solution.

(2) The consumption of $OH^-$ ions by the alkali–silica reaction significantly increases the concentration of $Ca^{2+}$ ions in the pore solution, because the saturation concentration of $Ca^{2+}$ ions is inversely proportional to the square of the concentration of $OH^-$ ions. The $Ca^{2+}$ ions preferentially react with the mature alkali silicate. Since the reaction accompanies the volume contraction of the product due to the release of the water of hydration and the cross-linking of silanol group, the mature alkali silicate converts to fragmental calcium alkali silicate. The fragmental calcium alkali silicate fills the pores to enhance the strength and to reduce the permeability of the concrete. The immature alkali silicate slowly reacts with $Ca^{2+}$ ions. The volume contraction is not so significant for the immature alkali silicate, so that the immature layer gradually converts to the tight layer of calcium alkali silicate called reaction rim. The aggregate is now packed with the reaction rim. The alkali hydroxide released from the alkali silicate by $Ca^{2+}$ ions further attacks the aggregate. The alkali hydroxide thus acts as a catalyst for the decomposition of aggregate. This is the reason why such a small amount of alkali (less than 1% by mass of cement) plays a significant role in ASR-induced deterioration of concrete.

(3) The reaction rim allows the penetration of alkali hydroxide into the aggregate, but not the extrusion of the resultant alkali silicate to the outside, so that the bulky alkali silicate is compressed in the aggregate and is finally released by cracking the reaction rim and the surrounding concrete. The expansive pressure stored in the aggregate is proportional to the relative amount of alkali silicate in the aggregate particles, or $U_A / U_S$. The maximum pressure is approximately given by $-\Delta G / V$, where $-\Delta G$ is the Gibbs free energy released by the formation of alkali silicate with volume $V$, and is two orders of magnitude higher than that necessary for cracking concrete.

(4) Addition of reactive aggregate causes the increase of the ASR expansion of concrete, because the added aggregate crack the concrete. However, too much addition suppresses the ASR expansion because of two reasons. One is the deficiency of $Ca(OH)_2$ used for the formation of reaction rims. Increase of the amount of the aggregate causes the increase of the consumption of $Ca(OH)_2$ by mature alkali silicate, so that the formation of reaction rims is suppressed. The other is the deficiency of alkali hydroxide for each aggregate particle. The expansive pressure stored in the aggregate particles is proportional to the relative amount of alkali silicate in the particles, so that the increase of the amount reduces the expansive pressure and suppresses crack formation. The ASR expansion thus decreases with increasing the amount of reactive aggregate after passing the pessimum proportion.

(5) The expansion also depends on the size of aggregate particles. When the total volume of aggregate particles is fixed, increase of the particle size decreases the total surface area of the aggregate and therefore decreases the amount of mature alkali silicate that does not contribute to the expansion. The

expansion therefore initially increases with the particle size. However, increase of the particle size significantly lowers the rate of ASR. Therefore, if significant amounts of alkali hydroxide and $Ca(OH)_2$ are consumed by co-existing ASR-tolerant aggregate, decrease of the particle size decreases the amount of alkali hydroxide and $Ca(OH)_2$ necessary for ASR. The pessimum size is thereby observed. The pessimum size effect is also observed if the ASR is not completed within the time of ASR measurement, because the ASR by larger aggregate is scarcely started while the ASR expansion by smaller aggregate is completed.

(6) Reactive aggregate with the size less than ~50 μm preferentially reacts with alkali hydroxide to convert to mature alkali hydroxide without leaving any reactive minerals. Homogeneous mixing of the sufficient amount of fine siliceous admixtures in concrete therefore inhibits the ASR by absorbing all the $Ca^{2+}$ ions that are necessary for the formation of reaction rims. The resultant fragmental calcium alkali silicate fills the pores in concrete to increase the strength and the durability of the concrete. The admixtures thus act as pozzolanic materials.

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