

## Inhibition of fly ash on the alkali silica reaction (ASR) in concrete with alkali-reactive sandstone as aggregate

Xu Lingling\*, Deng Min, Lan Xianghui

College of Materials Science and Engineering, Nanjing University of Technology, Nanjing City, P R China

### Abstract

Alkali aggregate reaction (AAR) is considered as the cancer of the concrete, which would destroy the concrete construction by the expansion of gels formed during the reaction between the alkali and reactive components bearing in aggregate. One of the effective measures to control the AAR is to add fly ash into concrete. This paper presents the effect of fly ash on alkali-silica reaction (ASR) of concrete in which alkali-active sandstone was used. The concrete added 30% fly ash replacing cement and with alkali content of 1.0kg/m<sup>3</sup>, 2.1 kg/m<sup>3</sup> and 3.0kg/m<sup>3</sup> were cured at 40°C, 80°C and 120°C, the expansion ratio and microstructure of concrete and content of soluble silica were tested. Then the reasonable mechanism of inhibition of fly ash on ASR is proposed that CSH gel with low Ca/Si is formed when fly ash is used to replace cement as binder in concrete, and found that low Ca/Si CSH gel has high capacity to combine the alkali so as to decrease the content of alkali reacted with sandstone. Meanwhile, the concrete with fly ash has modified pore structure that would prevent the diffusion of Na<sup>+</sup> and K<sup>+</sup> to reactive sandstone, resulting in low content of alkali to react with sandstone.

**Keywords:** alkali-silica reaction, fly ash, inhibition

## 1 INTRODUCTION

Alkali-silica reaction (ASR) is referring to the chemical reaction between alkalis from cement, supplementary cementitious materials (SCMs), aggregates, admixtures and poorly crystallized siliceous minerals contained in aggregates, resulting in ASR gel product which would be swelling to cause expansion and cracking of concrete. It is of importance to develop the measures to eliminate or reduce the possibility of ASR to ensure the safety of construction. Jinping hydraulic power station is site on the Yalong River, and concrete dam is as high as 305m. The aggregate chosen to make concrete has been tested by petrographic examination, and the results indicated that 5%-12% microcrystalline quartz is bearing in those metamorphosed quartz sandstone. Measuring by concrete prism test (CPT) and accelerated mortar bar test (AMBT) according to DL/T5151-2001, the aggregate has been proved alkali-reactive. To use those aggregate in dam concrete, the technique should be investigated to ensure no ASR taking place in concrete. The research results indicate that SCMs replacing for cement used in concrete can restrain ASR effectively[1,2,3]. In this paper fly ash is used to replace cement to eliminate the danger of ASR and the resulting effect and mechanism are studied.

## 2 MATERIALS AND METHODS

### 2.1 Cement and fly ash

---

\* Correspondence to: xll@njut.edu.cn

Moderate heat Portland cement P.MH42.5 with 0.54% Na<sub>2</sub>O<sub>eq</sub> produced by Ermei Cement Plant of Sichun Province is used in this project, whose chemical composition is listed in Table 1.

Fly ash is Class I from Baima Power Station of Neijiang City. The content of Na<sub>2</sub>O<sub>eq</sub> is 1.38%, and chemical composition is shown in Table 1.



## 2.2 Aggregate

Metamorphosed quartz sandstone marking as 8-4, 8-5 and DJ1 from Jinping were collected as aggregate of concrete for Jinping Hydropower Station. Petrographic examination indicated that 5%-12% microcrystalline quartz is bearing in those metamorphosed quartz sandstone. And they are proved alkali-reactive aggregate measured by concrete prism test (CPT) and accelerated mortar bar test (AMBT) according to DL/T5151-2001.

As a contrast aggregate, a nonreactive aggregate C was chosen from Yixing, which consists of quartz crystals with mosaic texture mainly and contains about 2% micro- to crypto-crystalline quartz, and the maximum value of expansion is 0.042% tested by CECS 48-1993, the expansive ratio is 0.096% and 0.131% at 14d and 28d tested as DL/T5151-2001 respectively, indicating relatively innocuous.

## 2.3 Mix proportions of concrete

Concrete prisms of 75mm×75mm×285mm were prepared as mix proportions shown in Table 2, where crushed stone are 5-20mm, ratio of sand is 30%, cement replacing by fly ash of 30% by weight. The content of Na<sub>2</sub>O<sub>eq</sub> in concrete was controlled as 1.0kg/m<sup>3</sup>, 2.1 kg/m<sup>3</sup> and 3.0 kg/m<sup>3</sup> by adding NaOH solution, respectively. Superplasticizer (SP) from Bote Company with the content of Na<sub>2</sub>O<sub>eq</sub> 13.83% was used to keep the workability of concrete. Then concrete prisms were cured in solution with the composition as same as that of pore solution of concrete corresponding to the each alkali content at 40°C, 80°C and 120°C, respectively.



## 3 RESULTS and DISCUSSION

Figure 1 shows the results of expansion of concrete prisms cured at 40°C, 80°C and 120°C, respectively. It is obvious that the expansion is increasing with the curing age, and with the content of alkali in concrete prisms at the same curing temperature, also with curing temperature when the same content of alkali contained. The expansion ratio of concrete prisms was not much different using aggregate 8-4, 8-5 and DJ1, relatively bigger for sandstone 8-5.

For concrete of alkali content 1.0kg/m<sup>3</sup> and using reactive aggregate, the curing days till the expansion ratio of concrete prisms smaller than 0.040% were 728 days at 40°C and 80°C, and 252 days at 120°C. For those of 2.1 kg/m<sup>3</sup>, they were 728 days at 40°C and 80°C, and 182 days at 120°C. And the curing time was 465 days at 40°C, 260 days at 80°C, and 75 days at 120°C when alkali content was 3.0kg/m<sup>3</sup> in concrete. Otherwise, the expansion ratio of concrete prisms was smaller than 0.040% when unreactive aggregate C was used curing 728 days at 40°C and 80°C, and 252 days at 120°C whatever alkali content 1.0kg/m<sup>3</sup>, 2.1kg/m<sup>3</sup> or 3.0kg/m<sup>3</sup>.

To clear the reaction between sandstone and alkali, solvating rate of SiO<sub>2</sub> was tested referring to ASTM C289-2003, where size of aggregate was 0.16-0.63mm, 25g aggregate was weighted and 250mL NaOH solution of concentration 1mol/L was added in each plastic container, then sealed and cured in water bath at 60°C and 80°C. The concentration of SiO<sub>2</sub> was measured based on the value of absorbance by spectrophotometer. Figure 2 shows the concentration of SiO<sub>2</sub> with curing age at 60°C and 80°C. The calculated soluble rate and reactive energy are listed in Table 3. It is obvious that the soluble rate constant is

much higher at 80°C than that at 60°C for each aggregate 8-4, 8-5 and DJ1, supporting that ASR reaction is faster at higher temperature and confirming with the results of microstructure observation.

The polished sections of concrete using aggregate of reactive sandstone DJ1 with different content of alkali cured in simulating solution at 80°C were observed using optical microscope. The photos shown in Figure 3 demonstrate that when alkali content is 1.0kg/m<sup>3</sup>, there are no cracking in concrete and better bonding between aggregate and mortar (see Figure 3(a)). For concrete with alkali content 2.1 kg/m<sup>3</sup> as seen Figure 3(b), no cracking takes place in concrete, but some white gelatinous substance was found in a little part of pores. By comparison, as shown in Figure 3(c) and 3(d), concrete cracks and some cracking are extending from the inner of aggregate to mortar, and some are stretching along the edge of aggregate. It is also found that some white gelatinous substance filled in cracking or pores. The white gelatinous substance consists of Si, K and Ca detected by SEM-EDS method and considered as alkali silica gel.

Figure 4 is the image and composition of element of CSH gel contained in pastes without or with 30% fly ash cured in simulating solution at 120°C for 14 days. The results confirm that Ca/Si ratio of CSH gel decreases from 1.55 to 1.24 as 30% fly ash replacing cement. When cement is replacing by fly ash till 45% in paste, the Ca/Si ratio of CSH is much lower as 0.67 tested by TEM-EDS method. The CSH gel with lower ratio of Ca/Si is considered having larger capacity of solidification of alkali[4]. The content of Na<sub>2</sub>O<sub>eq</sub> bound into CSH gel is 0%, 0.15% and 1.24% corresponding to the replacing amount of fly ash 0%, 30% and 45% in cement paste.

There are three combining forms of alkali into CSH gel. Alkali could be packaged in pores of CSH gel, and absorbed chemically on the surface of CSH gel, or solidification into the structure of CSH gel. The amount of alkali in CSH gel is affected by the quantity of Si-OH in CSH structure per volume of CSH gel. The quantity of Si-OH in CSH structure increases with decreasing of Ca/Si of CSH gel, and K<sup>+</sup> or Na<sup>+</sup> ions would enter the interlayer of CSH structure to occupy the sites of H of Si-OH originally, to form Si-OK or Si-ONa[5,6] resulting in bonding alkali strongly into CSH gel and reducing the amount of alkali to react with sandstone. This ASR restricting effect is much more enhanced by replacing cement by fly ash because of the pozzolanic reaction to producing CSH gel with lower Ca/Si which has larger specific surface area and has more Si-OH in structure.

#### 4 CONCLUSIONS

The expansion ratio of concrete prisms using sandstone as aggregate and adding 30% fly ash replacing cement and with alkali content of 1.0kg/m<sup>3</sup>, 2.1 kg/m<sup>3</sup> and 3.0kg/m<sup>3</sup> were increasing with temperature, alkali content and curing age. The solubility of SiO<sub>2</sub> of sandstone is much higher at 80°C than that at 60°C. The reasonable mechanism of inhibition of fly ash on ASR is proposed that CSH gel with low Ca/Si, which is formed when fly ash is used to replace cement as binder in concrete, has stronger capacity to combine the alkali because of its larger specific surface area and more Si-OH bonds in structure, in result decreasing the content of alkali reacted with sandstone.

#### 5 REFERENCES

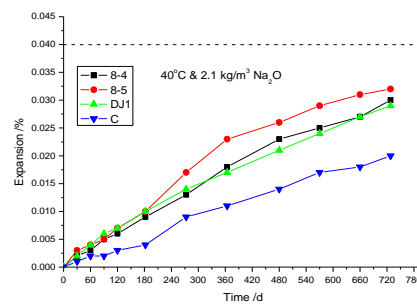
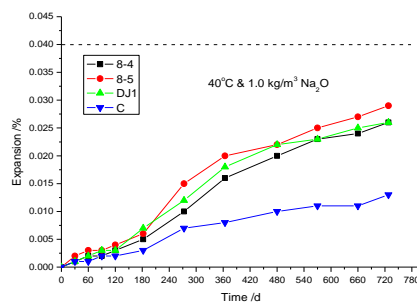
- [1] Medhat H S, and Michael D.A T (2002): Use of ternary blends containing silica fume and fly ash to suppress expansion due to alkali-silica reaction in concrete. *Cement and Concrete Research* (32):341-349
- [2] Michael T, Andrew D, and Philip N (2011): Effect of fly ash on the expansion of concrete due to alkali-silica reaction – exposure site studies. *Cement & Concrete Composites* (33):359-367

- [3] Robert D M, Amal R J, and Victor Y G (2010): Assessment of binary and ternary blends of metakaolin and Class C fly ash for alkali-silica reaction mitigation in concrete. Cement and Concrete Research (40):1664-1672
- [4] Wei FY (2005): Formation of CSH gel with low Ca/Si in paste and restrain of ASR. Ph.D dissertation to Nanjing University of Technology
- [5] Hong S Y, and Glasser F P (1999): Alkali binding in cement pastes part I. The C-S-H phase. Cement and Concrete Research (29):1893-1903
- [6] Hong S Y, and Glasser F P (2002): Alkali sorption by C-S-H and C-A-S-H gels part II. Role of alumina. Cement and Concrete Research (32):1101-1111

TABLE 1: Chemical composition of cement and fly ash /%									
sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	LOI	K <sub>2</sub> O	Na <sub>2</sub> O
cement	22.25	6.27	5.98	58.82	2.08	2.31	1.15	0.57	0.16
fly ash	48.21	22.47	13.25	4.93	1.70	2.16	4.26	1.72	0.25

TABLE 2: Mix proportion of concrete							
water/binder	Sand ratio /%	weight /kg/m <sup>3</sup>					
		water	cement	fly ash	sand	stone	SP
0.48	30	93	136.8	58.6	678	1582	1.173

TABLE 3: Soluble rate and reactive energy			
Aggregate	Soluble rate constant at 60°C /mmlo/L.d	Soluble rate constant at 80°C /mmlo/L.d	Ea /kJ/mol
8-4	0.26990	1.65543	88.63
8-5	0.21835	1.42729	91.74
DJ1	0.20489	1.46857	96.24



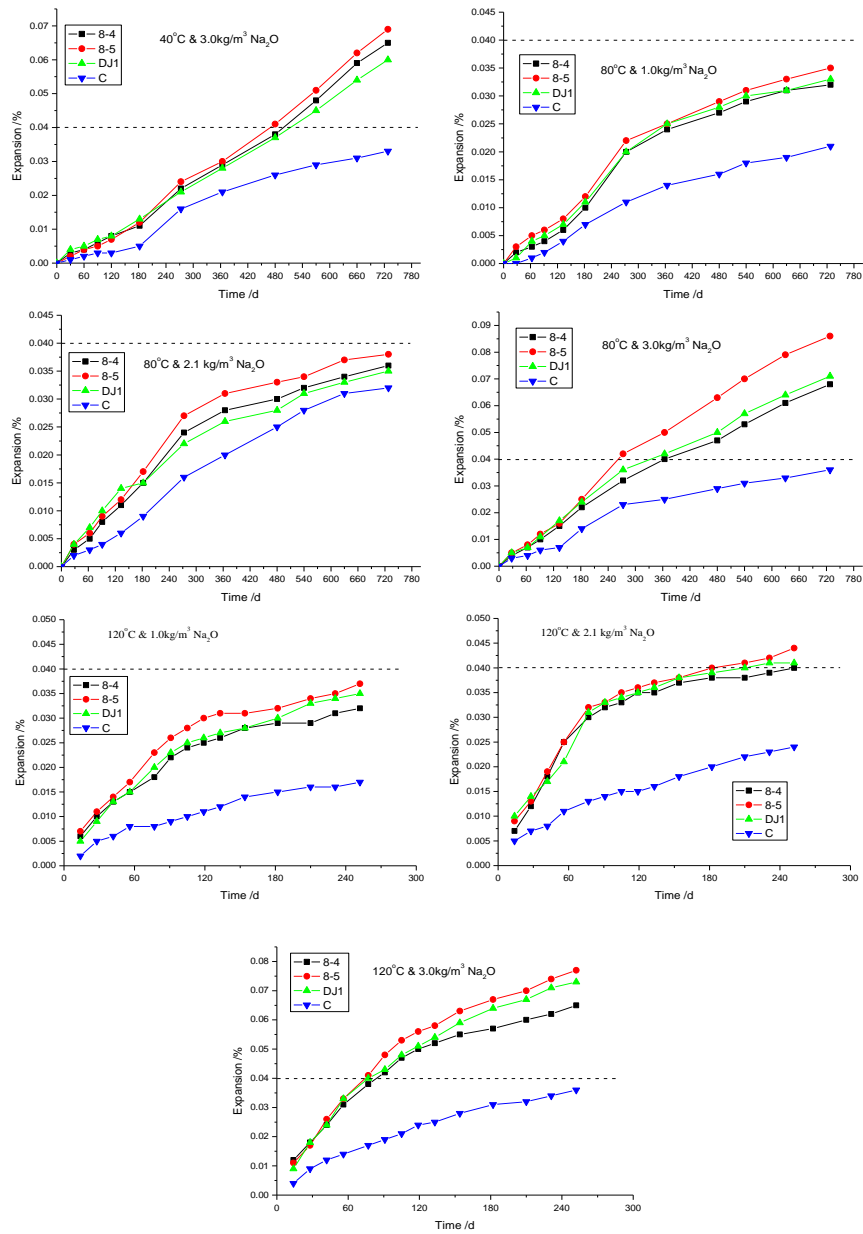


FIGURE 1: Expansion of concrete prisms with alkali 1.0kg/m<sup>3</sup>, 2.1kg/m<sup>3</sup> and 3.0kg/m<sup>3</sup> cured at 40°C, 80°C and 120°C

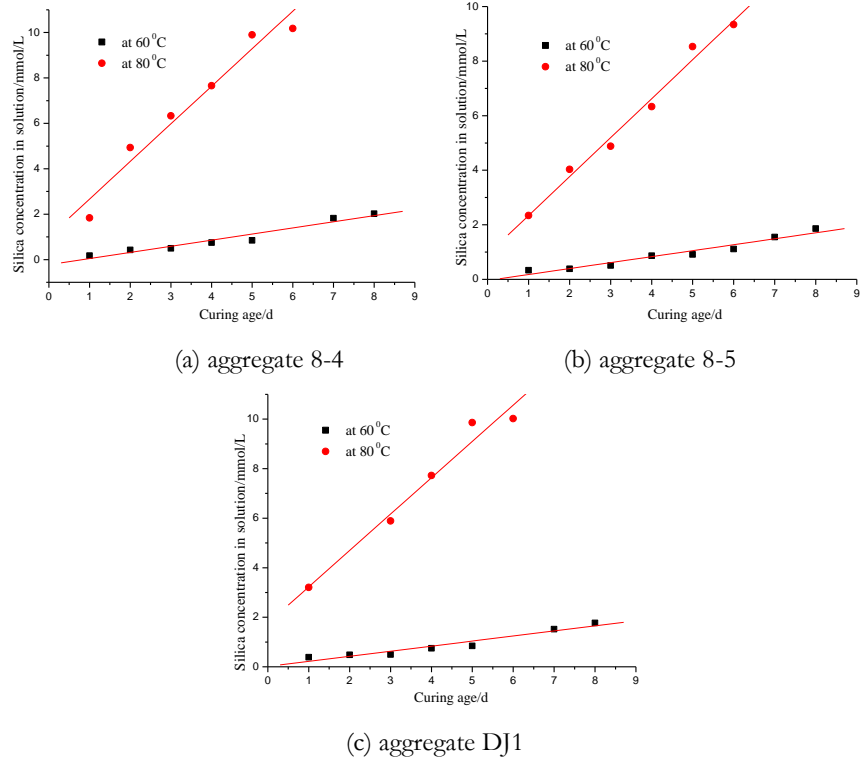


FIGURE 2: Silica concentration in solution of aggregates at 60°C and 80°C

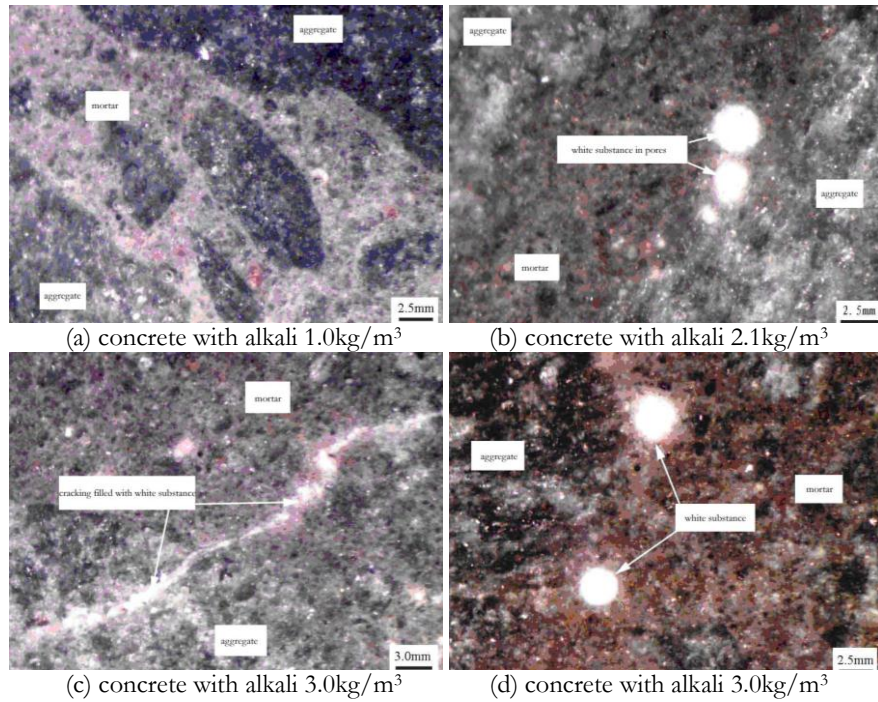


FIGURE 3: petrographic examination of concrete section with different alkali content

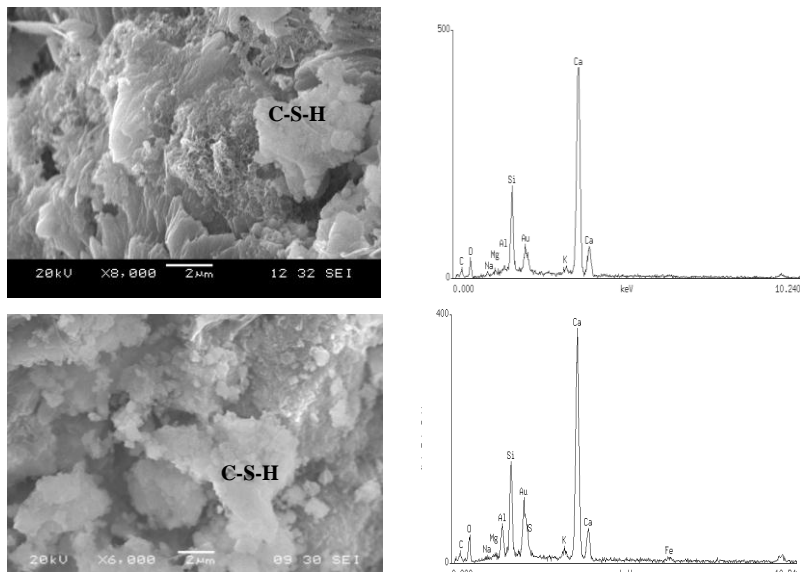


FIGURE 4: Image and composition of CSH gel in paste without fly ash (above) and 30% fly ash replacing cement (bottom) tested by SEM and EDS