

RELATION OF PHASE COMPOSITION OF CEMENT HYDRATES WITH SUPPLEMENTARY CEMENTITIOUS MATERIALS TO THE SUPPRESSING EFFECT ON ASR EXPANSION



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It is accepted around the world that the addition of an appropriate amount of a supplementary cementitious material (SCM) such as fly ash or blast furnace slag effectively suppresses mortar expansion caused by the alkali-silica reaction (ASR). However, even after extensive research, the actual suppression mechanism has yet to be identified and remains a matter of controversy.

Proposed mechanisms attribute the behavior to the hydration process and the phase composition of cement hydrates with SCMs present. The quantity and composition of the C-S-H gel are greatly affected by the type and amount of SCM. The addition of an appropriate amount of an SCM leads to the formation of C-S-H gel with a low Ca/Si ratio, resulting in lower concentrations of alkali and hydroxide ion in the pore solution, which is the most effective factor for ASR suppression. In order to evaluate the suppression effect of SCMs on ASR expansion, it is necessary to consider the hydration process of cement and SCMs as well as the properties of the cement hydrates.

Phase composition analysis such as X-ray diffraction (XRD) or Rietveld analysis is being developed as a promising method for measuring the reaction of cement hydrates including SCMs[1]. The combination of

XRD/Rietveld and selective dissolution allows mixed amorphous phases in hardened cement paste to be separated into C-S-H gel and the unhydrated glass phase of SCMs[2]. These techniques can be used to evaluate the relationship between the composition of cement hydrates and ASR expansion.

In this awarded paper, XRD/Rietveld analysis is combined with selective dissolution to measure the reaction of cement hydrates where SCMs have been added. Further, an accelerated mortar bar test is conducted to evaluate the suppression effect of SCMs on ASR expansion. By comparing the test results, the relationship between the composition of cement hydrates and the suppression of ASR expansion by SCMs is discussed.

Figure 1 shows the time dependency of each component in the OPC-R1 system. High temperatures such as 40°C accelerated the reaction of FA so that the reaction ratio of R1 reached approximately 30% at 7 days. The replacement of R1 slowed down the reaction ratio of belite while it accelerated C₃A and C₄AF. As a greater proportion of OPC is replaced by R1, the reaction of R1 slowed. This trend is in accordance with previous results[3].

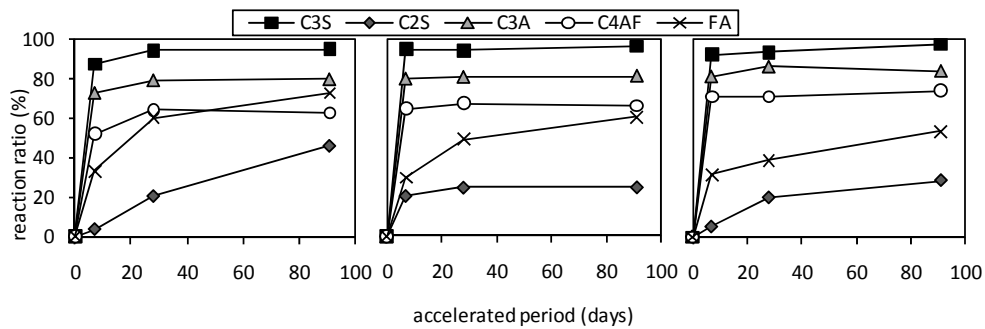


Figure 1 Time dependence of reaction ratio in the OPC-R1 system. From left to right, replacement ratio of OPC by R1 is 10, 20, and 30 vol%, respectively.

Figure 2 shows the reaction ratio of each mineral in OPC with different FA systems at 91 days. The reaction ratios of C₃S, C₃A and C₄AF are almost constant across all four systems, while the reaction ratios of C₂S and FA differ. Replacement of OPC with R2, which has moderate CaO content, results in a lower reaction ratio.

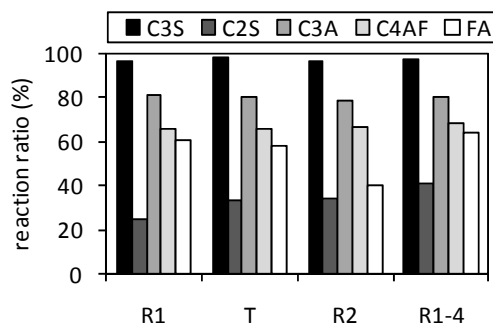


Figure 2 Effect of different FA systems (20vol%)

Figure 3 shows the reaction ratio of each mineral in the OPC-BFS system at 91 days in the accelerated test. The higher the BFS replacement ratio, the lower the reaction ratio of C₂S. On the other hand, the

reaction ratios of C₃A and C₄AF are higher with a higher BFS replacement ratio. These tendencies have also been reported in a previous paper[2].

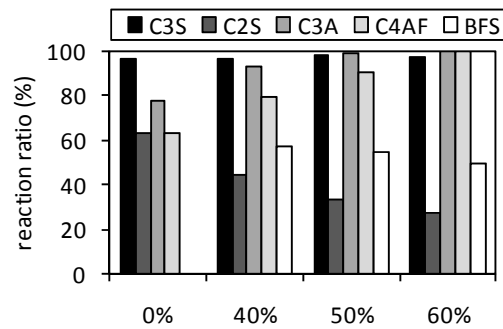


Figure 3 Effect of BFS replacement ratio (vol%)

Based on the XRD/Rietveld analysis and selective dissolution, the phase composition of the mixes is calculated. Figure 4 shows the phase composition of all the mix proportions and Table 4 gives the Ca/Si molar ratio of C-S-H gel at 91 days. The Ca/Si molar ratio of C-S-H gel in the absence of an SCM is larger than that given in the published data[4]. This may be attributed to the presence of amorphous Ca(OH)₂[5]. Although it is difficult to quantitatively evaluate the Ca/Si ratio of the C-S-H gel, variations in the ratio across the mix proportions can be obtained.

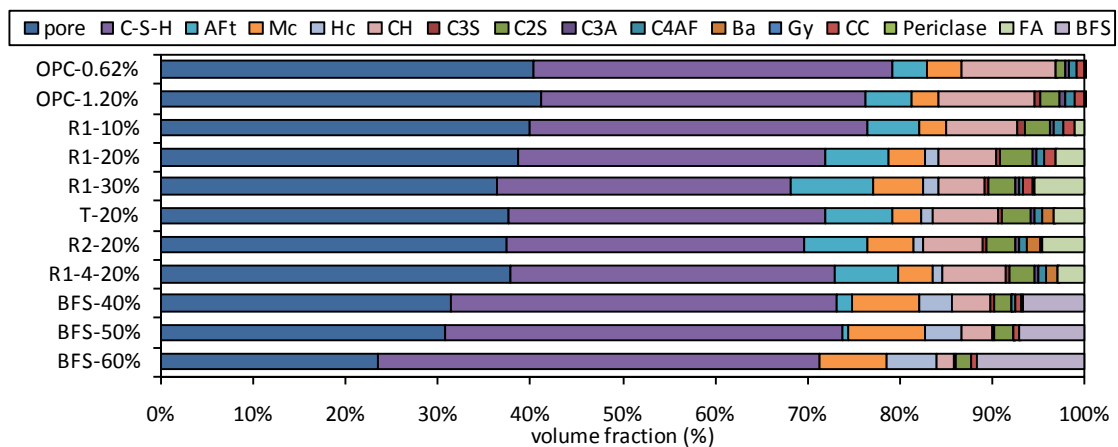


Figure 4 Phase composition of cement paste at 91 days

Table 1 Ca/Si molar ratio of C-S-H gel at 91 days

Type of SCM	OPC (Without SCM)	R1			T	R2	R1-4	BFS		
		10	20	30	20	20	20	40	50	60
Ca/Si molar ratio of C-S-H gel	2.21	1.85	1.48	1.18	1.62	1.66	1.51	1.65	1.53	1.45

This study focuses on alkali sorption on the C-S-H gel. The dilution effect of cement can be ignored because the total alkali content is held constant in all mixtures. Hong and Glasser previously conducted an alkali sorption experiment for C-S-H gel with a Ca/Si ratio ranging from 0.85 to 1.8 and showed equilibrium and the aqueous-solid phase balances [6]. The distribution ratio, R_d , can be calculated as:

$$R_d = R_s / R_l \quad (1)$$

where R_s is the alkali concentration in the solid C-S-H (mmol/g) and R_l is the alkali concentration in the solution (mmol/ml).

Figure 5 shows the sorption test results in the case of 300 mmol/l of NaOH solution, as conducted by Hong and Glasser [7]. Using the least squares method, Equation 2 is fitted to the test data:

$$R_d = \alpha (Ca/Si)^\beta \quad (2)$$

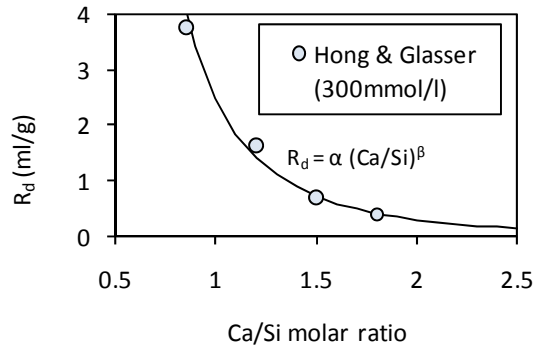


Figure 5 Ca/Si molar ratio of C-S-H and R_d

From this regression curve, α and β can be calculated as 2.47 and 3.05, respectively. The total alkali content per unit cement paste, C_{alkali} , can be calculated by:

$$C_{alkali} = R_s C_{CSH} + R_l C_{fw} \quad (3)$$

where C_{CSH} is the C-S-H content per unit cement paste, C_{fw} is the amount of free water per unit cement paste. C_{fw} is calculated by subtracting the combined water content in the crystalline phase from the initial free water content. Assuming equilibrium between the alkali in the solid and the liquid in the mortar, the alkalinity of the pore solution, R_l , can be obtained from Equations 1, 2 and 3. The hydroxide ion concentration of the pore solution can then be calculated even when SCMs are added in the mix, based on the composition of the C-S-H gel

Figure 6 shows the relationship between the calculated hydroxide ion concentration and the expansion ratio of the mortar with SCM. The expansion ratio increases linearly with increasing Ca/Si molar ratio in the C-S-H gel. These results strongly suggest that the mechanism by which an SCM suppresses ASR expansion is a reduction in the hydroxide ion concentration in the pore solution.

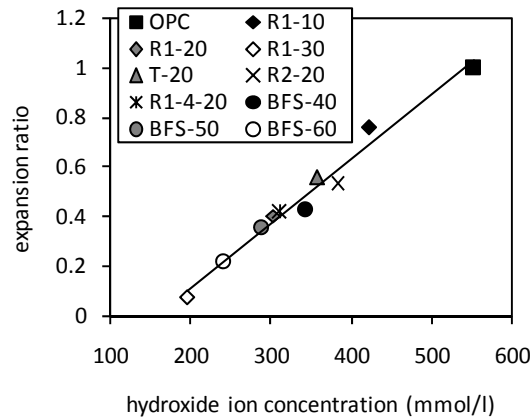


Figure 6 Calculated hydroxide ion concentration and expansion ratio

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