

THE EFFECT OF COMPOSITION OF CEMENT HYDRATES WITH SUPPLEMENTARY CEMENTITIOUS MATERIALS ON ASR EXPANSION

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Abstract

This study reports the suppression effect of supplementary cementitious materials (SCMs) based on the evaluated phase composition of SCM-added cement paste. X-ray diffraction (XRD) with Rietveld analysis and selective dissolution were applied for the evaluation. The effect of SCM type and replacement ratio on the phase composition of the system and the expansion of SCM-added mortar were investigated. The results showed that the addition of SCMs contributed to a reduced Ca/Si ratio of C-S-H gel. Calculation based on test results and published alkali sorption data revealed that the expansion of SCM-added mortar was closely correlated with the hydroxide ion concentration of the pore solution. Based on the test results, the suppression mechanism of SCMs is discussed.

Keywords: Supplementary cementitious materials, hydroxide ion concentration, XRD/Rietveld analysis, selective dissolution

1 INTRODUCTION

It is globally accepted that the addition of an appropriate amount of supplementary cementitious materials (SCMs) such as fly ash and blast furnace slag effectively suppresses mortar expansion caused by alkali-silica reaction (ASR). However, even with extensive research, the actual suppression mechanism has yet to be identified and remains a matter of controversy. The mechanism is considered to be related to the following factors:

- (1) Reduction in alkalinity of pore solution [1]
- (2) Consumption of calcium hydroxide [2]
- (3) Low permeability mainly due to densification of cement paste [2]

These changes in physical/chemical properties are attributed to the hydrating process and phase composition of SCM-added cement hydrates. In the case of C-S-H gel, its amount and composition were greatly affected by the type and amount of SCMs. The addition of an appropriate amount of SCMs 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 addition, the low Ca/Si ratio leads to an increased uptake of aluminium and alkali in the C-S-H gel when Al-including SCMs such as fly ash and blast furnace slag are mixed [3]. Calcium hydroxide is also consumed in the SCM reactions. These

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reactions increase the amount of C(-A)-S-H gel, resulting in the densification of hardened cement pastes. Therefore, in order to evaluate the suppression effect of SCMs on ASR expansion, it is necessary to consider the hydrating process of cement and SCMs and the properties of cement hydrates.

Phase composition analysis such as X-ray diffraction (XRD)/Rietveld analysis is being developed as a promising method for measuring the reaction of SCM-added cement hydrates [4]. The combination of XRD/Rietveld and selective dissolution method can separate the mixed amorphous phases in hardened cement paste to C-S-H gel and the unhydrated glass phase in SCMs [5]. These techniques can be used to evaluate the relationship between the composition of cement hydrates and ASR expansion.

In the present study, XRD/Rietveld analysis was combined with the selective dissolution method to measure the reaction of SCM-added cement hydrates, and an accelerated mortar bar test was 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 SCM suppression effect on ASR expansion is discussed.

2 EXPERIMENTS

2.1 Materials

Table 1 shows the chemical composition of the materials, including SCMs, used in this study. Ordinary Portland cement (OPC) with alkali content of 0.62 wt% was used as the base material. Four types of fly ash (FA) and one blast furnace slag (BFS) were prepared as SCMs. Table 2 shows the mineral composition of the FAs based on XRD/Rietveld analysis. Japanese BFS contains over 95% glass phase so the BFS used in this study was assumed to consist of glass phase only. The glass content of the fly ash was calculated from the determined crystal amount of added 10 wt% α -alumina as internal standard. SO_3 was assumed to exist in the form of anhydrite. The chemical composition of the glass phase in FA, shown in Table 3, was calculated by subtracting the chemical composition of the crystalline phase from the bulk chemical composition determined by X-ray fluorescence method by calibration curves. The results of fly ash characterization are summarized as follows:

- 1) The glass content and the alumina in the glass of "T" are significantly less than that in the other types of FA because of high mullite content;
- 2) "R2" contains approximately 10% CaO in the glass phase, although its glass content is 80%;
- 3) The chemical/physical properties of R1 and R1-4 are almost the same, while the glass content of R1 is 10% higher than that of R1-4.

For the accelerated mortar bar test, artificial glass was used as the reactive aggregate. The aggregate was crushed and ground in order to satisfy the particle size distribution specified in ASTM C 227. According to ASTM C 289, the dissolved silica "Sc" and the reduction in alkalinity "Rc" was 609mmol/l and -173 mmol/l, respectively.

2.2 Mixture proportions

Cement paste

Cement paste was prepared with a water-to-cement ratio of 0.50. Sodium hydroxide solution was added to the cement so that the $\text{Na}_2\text{O}_{\text{eq}}$ of the cement was 1.20 wt%. Cement paste without adding sodium hydroxide solution was mixed for comparison. FA was mixed at 10, 20 and 30% by volume of cement. BFS was mixed at 40, 50 and 60% by volume of cement. Sodium hydroxide solution was added to control the total alkali content in SCM-added mortar equal to that of the mortar without SCM. In calculating the total alkali content in the cement paste, the SCM alkali content was not considered. Therefore, the physical effect of lowering the total alkali content in mortar by adding SCMs can be ignored.

Mortar

Mortar without SCMs was mixed so that the water-to-cement ratio and sand-to-cement ratio were 0.50 and 2.25, respectively. Sodium hydroxide solution was added to the cement so that the $\text{Na}_2\text{O}_{\text{eq}}$ of the cement was 1.2% by mass. The SCM replacement ratio and calculation of total alkali content were set to be the same as for the cement paste. In calculating the total alkali content in the mortar, the SCM alkali content was not considered. Therefore, the physical effect of lowering the total alkali content in the mortar by adding SCMs was not considered. The aggregate content and water content per unit mortar were kept constant in all mix proportions. Also, the total alkali content per unit mortar was the same in the mixture proportions of mortar.

2.3 Hydration analysis

Sample preparation

Cement paste was mixed for 3 min in a Hobart mixer. After one day of hydration, the mixed paste was stored in sealed containers at 40°C for 7, 28 and 91 days. At each age, hydration was stopped by immersing the crushed paste in acetone and storing the specimen under RH 11% at ambient temperature in N_2 gas purged chamber for 7 days before being analyzed.

XRD/Rietveld analysis

XRD measurement and Rietveld analysis were conducted according to the method of Hoshino *et al.* [5]. The sample measured by XRD was prepared by mixing a paste for which hydration was stopped by immersing in a large amount of acetone and 10 mass% $\alpha\text{-Al}_2\text{O}_3$ (corundum) with an average particle size of 0.4 μm . The measurement conditions for XRD were tube voltage of 50 kV, tube current of 250 mA, scan range of $2\theta = 5\text{--}65^\circ$, step width of 0.02° and scan speed of $2^\circ/\text{min}$. TOPAS software (Bruker AXS) was used for Rietveld analysis. The quantified phases were calcite (CC), gypsum (Gy), bassanite (Ba), portlandite (CH), ettringite (Ett), monosulfate (Ms), monocarbonate (Mc), and hemicarbonates (Hc) depending on the sample, as well as basic minerals such as alite (C_3S), belite (C_2S), cubic C_3A , orthorhombic C_3A , and C_4AF . The amount of C_3A was calculated as the sum of both phases detected by Rietveld analysis. The amount of amorphous phase was calculated by:

$$G = 100 \times (A - R) / [A \times (100 - R) / 100] \quad (1)$$

where G is the amount of amorphous phase (mass%), R is the added ratio of corundum (mass%), and A is the measured value of corundum (mass%). As the SCMs contain a large amount of amorphous phase, the C-S-H gel content was obtained by subtracting the unhydrated amorphous phase in SCMs from the calculated amorphous phase content.

The hydration ratio of each mineral, R_x , was calculated by:

$$R_x = \frac{H_x}{[C_x \times (100 - \text{LOI})] \times 100} \times 100 \quad (2)$$

where C_x is the initial amount in unhydrated cement (mass%), H_x is the quantified amount of mineral after hydration (mass%), and LOI is the loss on ignition (mass%).

The accuracy of XRD/Rietveld analysis was reported in another paper [5].

Selective dissolution

In order to measure the reaction ratio of FA, the selective dissolution method using 2 mmol/l HCl and 5% Na_2CO_3 solution was adopted [6]. To evaluate the BFS reaction ratio, the salicylic acid – acetone – methanol – acetone – methanol method was used to quantify the amount of BFS [7].

2.4 Accelerated mortar bar test

Mortar specimens were left in their molds for 24 h after casting. Then, they were removed from the molds and the initial length was measured. After precuring, the specimens were placed in a fog container, which was maintained at a temperature of 40°C and RH of 100% for 91 days. Length change was measured at 20°C after precooling at weekly intervals.

2.5 Pore solution analysis

Pore solutions of mortar without SCMs, which differed in total alkali content, were expressed using a high-pressure apparatus. Then, the hydroxide ion concentration was measured by titration. Pure limestone with more than 95 wt% of calcite was used as a non-reactive aggregate ($Sc = 3 \text{ mmol/l}$, $Rc = 23 \text{ mmol/l}$).

3 RESULTS AND DISCUSSION

Hydration of cement without SCMs

Figure 1 shows the time dependency of each mineral in OPC with added alkali. Due to the high temperature, each mineral component showed high reactivity. The reaction ratio of alite was 90% at 7 days while that of belite was 18%. Thereafter, the alite reaction terminated while belite showed a slow reaction. Compared to the published results for cement hydration at 40°C [e.g., 8], the reaction ratio of belite was significantly low. The difference between the experiment in the present study and the published experiments is mainly the addition of NaOH. Figure 2 shows the reaction ratio of cement with and without the addition of NaOH solution at 91 days. NaOH addition reduced the reaction ratio of each cement component, especially belite. The high hydroxide ion concentration lowered the Ca^{2+} ion concentration in the pore solution. This effect terminated the reaction of each component under supersaturated conditions. Especially, the dissolution process of belite depends on Ca^{2+} ion concentration so that the addition of NaOH solution reduced the belite reaction ratio.

Hydration of cement with FA

Figure 3 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 approximately 30% of the reaction ratio of R1 could be observed at 7 days. The replacement of R1 slowed down the reaction ratio of belite while it accelerated C_3A and C_4AF . High replacement of OPC by R1 decreased the reaction of R1. This trend was in accordance with Hanehara *et al.* [9].

Figure 4 shows the reaction ratio of each mineral in OPC with different FA systems at 91 days. Alite, C_3A and C_4AF showed almost the same reaction ratios in all the systems, while the reaction ratios of belite and FA differed. R2, which has moderate CaO content, showed a low reaction ratio.

Hydration of cement with BFS

Figure 5 shows the reaction ratio of each mineral in the OPC-BFS system at 91 days of the accelerated period. The higher the BFS replacement ratio, the lower the belite reaction ratio. On the other hand, C_3A and C_4AF showed a higher reaction ratio with a higher BFS replacement ratio. These tendencies were reported in the previous paper [5].

Phase composition of SCM-added cement paste

Based on the XRD/Rietveld analysis and selective dissolution, the phase composition of the mix was calculated. In converting the mass fraction of each component to the volume, the density of each component was obtained from previous literature [5, 10]. The density of C-S-H gel, ρ_{CSH} , was calculated in accordance

with the following Equation 3 proposed by Suda *et al.* [11]. From the material balance between the reacted components and produced hydrates, the Ca/Si molar ratio of C-S-H can be calculated.

$$\rho_{CSH} = 0.241Ca/Si + 1.72 \quad (3)$$

Figure 6 shows the phase composition of all the mixture proportions and Table 4 shows the Ca/Si molar ratio of C-S-H gel at 91 days. The Ca/Si molar ratio of C-S-H gel without SCMs was larger than that of published data [10]. This may be attributed to the presence of amorphous Ca(OH)₂ [12]. Although it is difficult to quantitatively evaluate the Ca/Si ratio of C-S-H gel, the difference in the ratio for each mixture proportion can be compared.

In the OPC-R1 system, as shown in Figure 6, C-S-H content was almost constant independent of the R1 replacement ratio, while CH content was significantly decreased. Hc was detected at over 20% R1 replacement ratio. Regarding the effect of FA type, the C-S-H content of R2, moderate-Ca FA, was much less than with the other types of FA. On the other hand, T, which contains less glass, showed the largest CH content as shown in Figure 6, which means that the consumption of CH was small compared to that in R1 and R1-4 at a given reaction ratio of FA as shown in Figure 4. The combination of FA reaction ratio and consumed Ca(OH)₂ significantly affected the Ca/Si ratio of C-S-H gel. T and R2 showed a larger Ca/Si molar ratio than that of R1 and R1-4 as shown in Table 4. However, it should be noted that a drastic decrease in Ca/Si molar ratio was observed when cement was replaced with FA.

In the OPC-BFS system, the most distinctive change was the increase in C-S-H content as shown in Figure 6. Due to the high CaO content in BFS, the decrease in Ca/Si molar ratio was less compared with that for FA as shown in Table 4. The Ca/Si molar ratio of BFS-60 was almost the same as with R1-20, while the C-S-H content of BFS-60 was significantly larger than that of R1-20.

Suppression effect of SCMs on ASR expansion

Table 5 shows the expansion ratio of the SCM-added mortar. Expansion ratio is defined as the ratio of expansion of mortar with SCM to that of mortar without SCM. R1-30 was the most effective for suppressing ASR expansion in all the mixture proportions. Focusing on the effect of FA type, T and R2 were less effective than R1 and R1-4 because they contain less glass and a high CaO content. The expansion ratio of BFS-50 was the same as that of R1-20. These trends regarding the suppression effect of SCMs are similar to those reported in previous papers [13].

Calculation of alkalinity of pore solution based on phase composition

The replacement of OPC by SCMs significantly reduced the alkali and hydroxide ion concentrations in the pore solution. The mechanism can be attributed to the dilution of cement, consumption of portlandite and alkali sorption by C-S-H gel with low Ca/Si. In addition, Al-substitution in C-S-H can fix alkali because aluminium can incorporate into C-S-H mainly at the bridging sites in the silicate chains [3]. The fixed amount in C-A-S-H gel is significantly larger than that in C-S-H when the Ca/Si ratio is the same [14].

This study focused on the alkali sorption on C-S-H gel because the efficiency of Al-substitution on alkali fixation is not obvious. The dilution effect of cement can be ignored because the total alkali content was kept constant in all mixtures. Hong and Glasser 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, aqueous-solid phase balances [15]. From the test results, the distribution ratio, R_d , can be calculated as:

$$R_d = R_s/R_l \quad (4)$$

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

Figure 7 shows the sorption test results in the case of 300 mmol/l of NaOH solution, as conducted by Hong and Glasser [15]. Equation 5 was fitted to the test data by the least squares method:

$$R_d = a(Ca/Si)^\beta \quad (5)$$

From the regression curve shown in Figure 7, a and β can be calculated as 2.47 and 3.05, respectively. Total alkali content per unit cement paste, $C_{alkalis}$, can be calculated by:

$$C_{alkali} = R_s C_{CSH} + R_l C_{fw} \quad (6)$$

where C_{CSH} is the C-S-H content per unit cement paste, C_{fw} is the 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 that the interaction of alkali between solids and liquids in the mortar is assumed in equilibrium, the alkalinity in the pore solution, R_l , can be obtained from Equations 4, 5 and 6.

For verification, the calculated results (*Calc.*) were compared to the experimental results (*Exp.*) by measuring the high-pressure extraction of pore solution. In the calculation, it was assumed that the counter ion of alkali is hydroxide ion. It was also assumed that the alkali concentration was not affected by the presence of pure limestone aggregate, as shown in Duchesne and Berube [16]. Figure 8 shows the relationship between the calculation and experiment. The calculated results were approximately 80% of the value of the experimental results. The reason for this difference may have been the difference in solid-to-liquid ratio, concentration of solution, temperature and so on.

Relationship of calculated hydroxide ion concentration, phase composition of cement hydrates to ASR expansion

Figure 9 shows the relationship between the calculated hydroxide ion concentration and the expansion ratio of the SCM-added mortar. The expansion ratio increases linearly with the increase in Ca/Si molar ratio of C-S-H gel. This result indicates that the reduction in alkalinity of the pore solution is the dominant mechanism for suppressing ASR expansion. This mechanism is strongly supported by numerous researchers [1, 13, 17-18].

At a given total alkali content in mortar/concrete, the reduction in alkalinity of pore solution is attributed to the amount of C-S-H gel and its composition, especially the Ca/Si molar ratio. When cement was replaced with an appropriate amount of FA, a certain decrease in Ca/Si molar ratio could be attained while the C-S-H content was almost the same as that without SCMs. On the other hand, when an appropriate amount of BFS was mixed in with the cement, the C-S-H content increased greatly because of the high reactivity of BFS although the Ca/Si molar ratio hardly decreased compared to that with FA.

From these results, it can be concluded that the replacement of cement with SCM changes the hydration of the cement and the SCM itself, resulting in a decrease in Ca/Si molar ratio and an increase in the amount of C-S-H gel, which contributes to the suppression of ASR expansion.

4 CONCLUSIONS

This study reported the suppression effect of SCMs based on the evaluated phase composition of SCM-added cement paste. The following conclusions can be drawn based on the test results:

- (1) Replacement of cement with SCMs changes the hydration of the cement and the SCM itself, resulting in a change in the composition and the amount of hydrates formed.
- (2) Mixing in an appropriate amount of fly ash contributes to a decreased Ca/Si molar ratio of C-S-H gel while the C-S-H content is almost the same as that without SCMs. On the other hand, mixing in an appropriate amount of blast furnace slag increases the C-S-H content formed, although the Ca/Si molar ratio hardly decreases compared with that for the fly ash.
- (3) A calculation method for evaluating the alkalinity of the pore solution by using C-S-H content, Ca/Si molar ratio, free water content, and initial total alkali content was proposed. The proposed calculated

alkalinity of pore solution was approximately 80% of the value obtained from the experiment in which the pore solution was extracted by high-pressure apparatus.

- (4) The calculated alkalinity of the pore solution in the SCM-added mortar was closely correlated to the ASR expansion of the mortar. This result proved also theoretically that the reduction in alkalinity of pore solution is the dominant mechanism for suppressing ASR expansion as reported by former researches.

5. ACKNOWLEDGEMENT

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TABLE 1: Chemical composition of materials.

Chemical composition (wt%)	OPC	FA				BFS
		R1	T	R2	R1-4	
LOI	0.6	1.5	1.58	1.56	2.25	0.11
SiO ₂	21.79	60.17	61.16	51.96	59.05	33.64
Al ₂ O ₃	4.98	22.24	29.69	20.09	23.72	14.97
Fe ₂ O ₃	2.91	4.29	2.7	5.85	4.33	0.17
CaO	65.23	5.8	0.75	13.78	5.12	42.83
MgO	1.21	1.66	0.59	2.17	1.36	5.71
Na ₂ O	0.31	0.48	0.18	0.78	0.44	0.31
K ₂ O	0.47	0.97	0.34	1.22	0.87	0.24
SO ₃	1.72	0.79	0.12	1.22	0.63	0.05
P ₂ O ₅	-	0.81	0.42	0.59	0.72	0.01
Total	99.22	98.71	97.53	99.22	98.49	98.04

TABLE 2: Mineral composition of fly ash by XRD/Rietveld analysis.

	R1	T	R2	R1-4
Quartz	7.6	18.6	5.9	10.2
Mullite	15.6	37.9	9.0	21.2
Magnetite	0.3	0.3	0.5	0.6
Hematite	0.3	0.9	0.5	0.4
Lime	0.1	0.0	0.4	0.3
Portlandite	0.1	0.0	2.0	0.3
Calcite	0.2	0.0	0.0	0.0
Periclase	0.2	0.0	0.3	0.3
Rutile	0.0	0.5	0.0	0.1
LOI+Moisture	1.4	1.6	1.1	2.2
Glass	70.0	38.8	75.2	60.7

TABLE 3: Chemical composition of glass in fly ash.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	Total
R1	48.14	11.06	3.65	3.77	1.42	0.48	0.97	0.81	70.3
T	31.86	2.51	1.5	0.15	0.59	0.18	0.34	0.42	37.55
R2	43.56	13.64	4.85	9.71	1.84	0.78	1.22	0.59	76.18
R1-4	42.86	8.47	3.31	3.12	1.08	0.44	0.87	0.72	60.87

Type of SCM	OPC (Without SCMs)	R1			T	R2	R1-4	BFS		
Replacement ratio (vol%)		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

OPC	R1-10	R1-20	R1-30	T-20	R2-20	R1-4-20	BFS-40	BFS-50	BFS-60
1.00	0.76	0.40	0.08	0.56	0.54	0.42	0.43	0.36	0.22

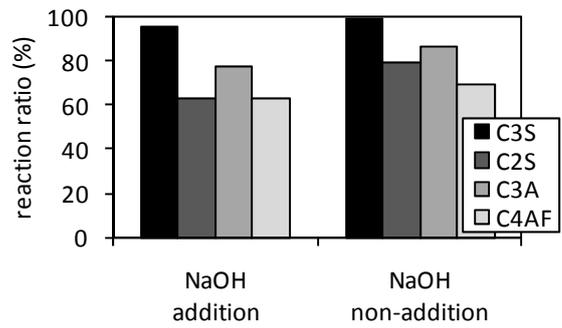
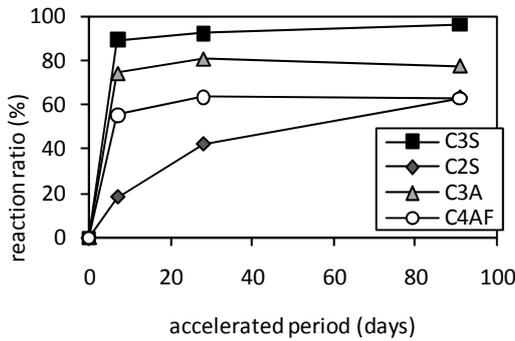


FIGURE 1: Time dependency of OPC reaction ratio.

FIGURE 2: Effect of NaOH addition.

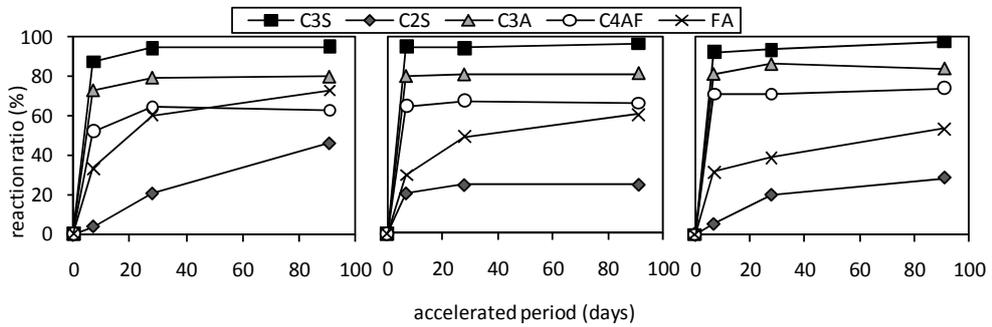


FIGURE 3: Time dependency of reaction ratio in the cement-R1 system. From left to right, replacement ratio was 10, 20, and 30 vol% respectively.

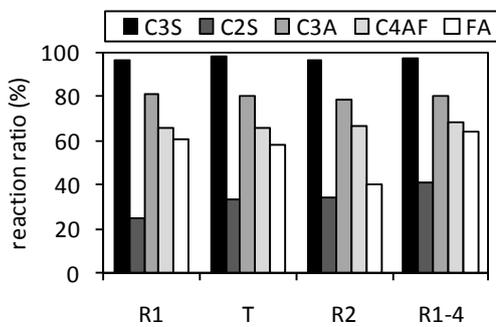


FIGURE 4: Effect of fly ash characteristics.

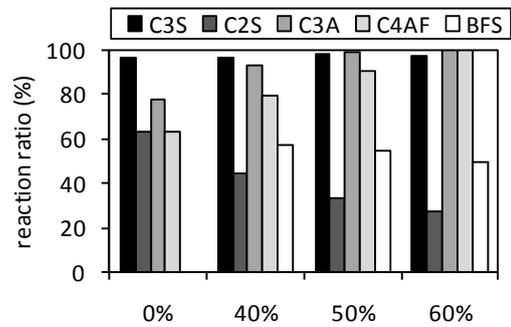


FIGURE 5: Effect of BFS replacement ratio (vol%).

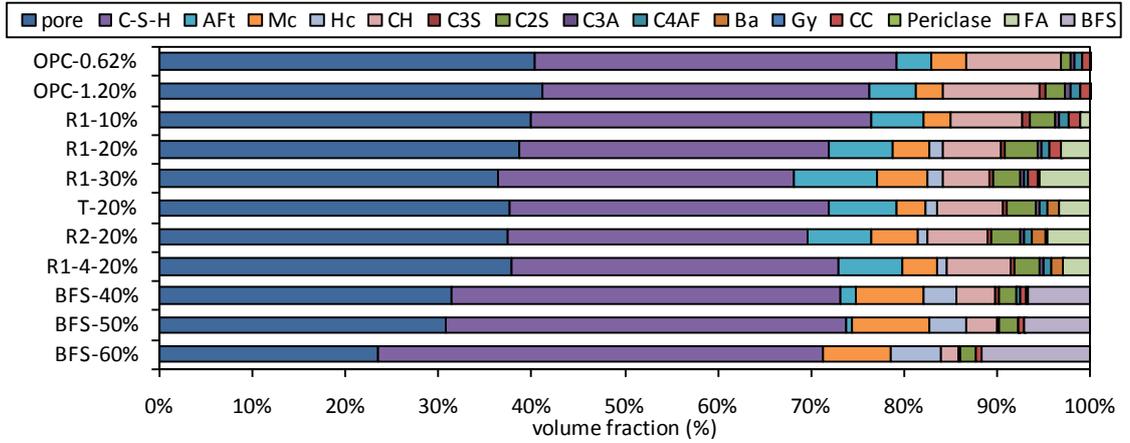


FIGURE 6: Phase composition of cement paste at 91 days.

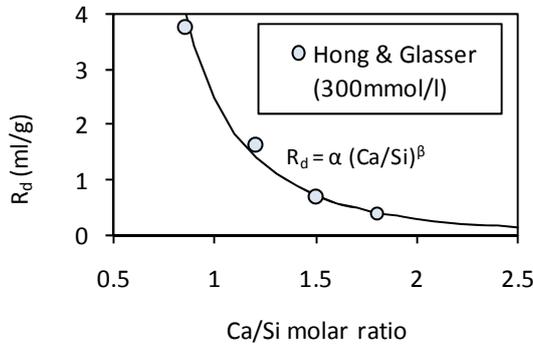


FIGURE 7: Ca/Si molar ratio of C-S-H and R_d .

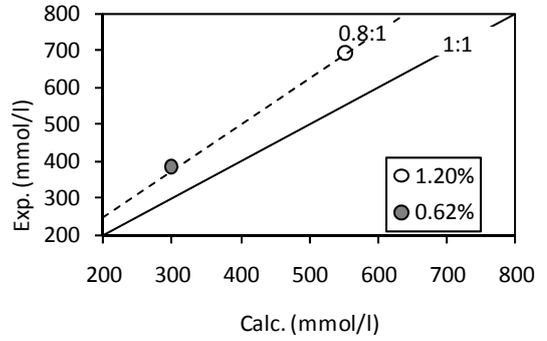


FIGURE 8: Relationship between calc. and exp.

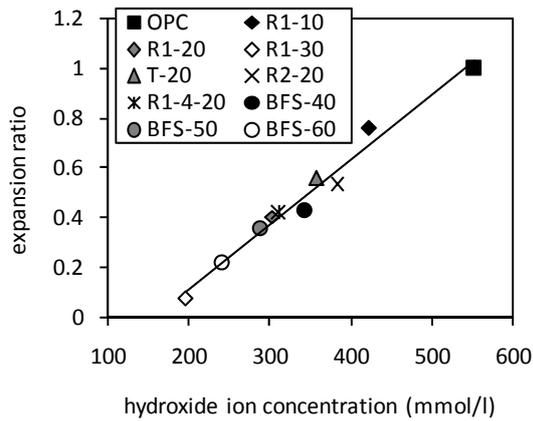


FIGURE 9: Calculated hydroxide ion concentration and expansion ratio.