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Use of ternary blends containing high calcium fly ash and slag to mitigate sulphate attack

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High Calcium fly ash is known to have adverse effect if used in concrete exposed to sulphate attack. In this study, high calcium fly ash is used with slag in ternary blends in an attempt to enhance sulphate resistance. This study used ASTM C 1012 mortar bar test to evaluate sulphate resistance. Mortar bars were made with 100% Portland cement mix (control mix), binary blends of either high calcium fly ash or slag, and the ternary blends thereof. The expansions were monitored up to 2 years. The expansion levels of ternary blends and binary blends of same level of supplementary cementing materials (SCMs) were compared. Evaluated ternary blends showed to have enhanced resistance against sulphate attack. The study further investigated the role of ion diffusion, and calcium hydroxide depletion in controlling the sulphate attack of binary and ternary blends.

Keywords: high calcium fly ash, slag, ternary blend, sulphate attack, permeability, calcium hydroxide, supplementary cementing materials

1 Introduction

High calcium fly ash (HCFA) is less effective in comparison to low calcium fly ash in controlling sulphate attack in concrete (Tikalsky et al., 1990; Tikalsky and Carrasquillo 1992; Shashiprakash and Thomas, 2001; Shehata and Thomas, 1999). In fact, high calcium fly ash has shown adverse effect under sulphate exposure (Shashiprakash and Thomas, 2001). High calcium and high aluminasilicate glass contents of ASTM Class C fly ash are referred to as the dominant factors causing adverse effect in sulphate (Shehata and Thomas, 1999; Tikalsky and Carrasquillo, 1992, 1993).

As a way to enhance the performance of high calcium fly ash against sulphate attack, few researchers added gypsum along with high calcium fly ash (Freeman and Carrasquillo, 1995; Shehata et al., 2008). The additional sulphate ions in the form of gypsum consume calcium aluminates during early hydration of the cementing materials leaving less aluminate for the late formation of sulphoaluminate phases associated with sulphate attack (Shehata et al., 2008; Thomas et al., 1999). Shehata et al. (2008) showed that adding small amount of silica fume (3% - 5%) along with high calcium fly ash (20% - 30%) has significant reduction in expansion of mortar bars exposed to sulphate solution.

In this paper, slag blended with HCFA was used in order to investigate the effect of ternary cementing system containing slag/HCFA. It was hoped that the ternary blends of high calcium fly ash and slag may result in synergistic effects in terms of resisting sulphate attack. One way by which slag reduces the sulphate expansion is by binding the Al^{3+} into C-S-H (Gollop and Taylor, 1996; Wee et al., 2000). For instance, Shehata et al. (2008) showed 30% replacement of Canadian slag is sufficient to suppress the sulphate attack mortar bar expansion below 0.1% at one year. Hence, the ability of slag to bind Al^{3+} could be expected to compensate for the adverse effect of high calcium fly ash due to its higher calcium aluminate phases. This is investigated in this paper.

2 Materials

Ottawa sand, General Use Portland cement (PC), one high calcium fly ash (FA), and one slag were used in these experimental specimens. Table 1 lists the chemical composition of the cementing materials used in this study.

Table 1: Chemical composition of cementing materials

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	P_2O_5	S.G.
PC	19.58	5.35	2.29	62.84	2.43	4.1	1.13	0.21	0.31	0.11%	3.15
FA	33.72	18.47	7.04	27.16	5.08	2.84	0.33	1.72	1.41	0.91%	2.65
Slag	34.4	7.4	0.94	43.2	9.3	0.83	0.58	0.57	0.44	175ppm	2.94

3 Experimental Details

3.1 Mortar Bars

ASTM C 1012 was followed to measure the expansion of mortar bars exposed to 5% Na_2SO_4 solution up to 2 years. Mortar is prepared as per ASTM C 305. Stainless steel studs were attached on both ends to enable the measurements. The expansion of the mortar bars was taken at 1, 2, 3, 4, 8, 12, 13, 15, 26, 39, 52, 78, and 104 weeks. The length measurements were taken with reference to a standard invar bar and expressed as percentage of the original length. Table 2 lists the proportions of the cementing materials incorporated in the tested mortar bars.

Table 2: Blends prepared to evaluate sulphate susceptibility

Mix ID	**PC (%)**	**FA (%)**	**Slag (%)**
Control	100	-	-
20% FA	80	20	-
40% FA	60	40	
20% Slag	80	-	20
30% Slag	70	-	30
40% Slag	60	-	40
15/15	70	15	15
20/20	60	20	20
30/30	40	30	30
20/30	50	20	30
20/40	40	20	40
40/20	40	40	20

3.2 Thermal Gravimetric Analysis

Paste samples were prepared at the same cementing materials combinations shown in Table 2 using a high-speed, high-shear food blender. The w/c was kept 0.5 for all the samples. The prepared paste blends were poured into plastic moulds of 50 mm diameter and 100 mm height and cured at 100% relative humidity and 35 ^{o}C for the first 24 hours. Then, the samples were de-moulded and soaked into limewater at 23^{o}C for another 27 days. After that, the samples were taken out of limewater and broken into pieces and soaked into alcohol for 1 week. Then, the samples were stored in the oven at 80^{o}C until the day of analysis. On the day of running TGA, the fragments were taken out of the oven and screened through the 1.18 mm sieve. Analysis was carried using the instrument AutoTGA 2950HR V6.1A on the paste power passed through 1.18 mm sieves.

3.3 Rapid Chloride Permeability Test

ASTM C1202 – Rapid Chloride Permeability Test was conducted on the corresponding mortar mixes of the sulphate attack mortar bars. Though ASTM C1202 is intended for testing concrete specimens, it is adapted in this study for mortar mixes. Mortar mixes were prepared according to ASTM C 305 and cast into the standard cylinders in three layers, each layers compacted 25 times with the steel rod. At the time of testing, the cylinders were cut into 50 mm thick specimens, and the average RCPT values obtained from two specimens are reported here.

4 Results

4.1 Mortar Bar Expansion

The expansion of mortar bars submerged in 5% Na_2SO_4 solution and monitored for 2 years. The results are analysed for the performance of binary and ternary blends and effect of SCM on the expansion.

4.2 Expansion of Binary Blend Mortar Bars

Binary blends tested include blends containing HCFA and blends with slag. Figures 1 and 2 present the expansion of fly ash and slag blends, respectively. The 40% fly ash mix broke before 4 months while 20% fly ash specimens lasted slightly longer than 4 months. Replacing PC with Class CH fly ash did not improve the sulphate resistance; instead it has worsened the durability. This behaviour is reported elsewhere and commonly attributed to high calcium content, and tendency to form monosulphate prior to exposing to the sulphate solution (Shashiprakash and Thomas, 2001; Freeman and Carrasquillo, 1995).

On the other hand, binary blends of slag performed well. 20% slag replacement reduced the expansion dramatically compared to the control mix. The 30% and 40% slag replacements further reduced the expansion below ASTM 6-month and 1-year limits of 0.05% and 0.1%. The superior performance of slag blends is attributable partly to the ability to incorporate Al^{3+} ions into its C-S-H (Gollop and Taylor, 1996). In addition, high-calcium fly ash contains calcium-aluminate phase that is susceptible to sulphate attack (Shehata et al., 2008).

4.3 Expansion of Ternary Blend Mortar Bars

Figure 3 shows the expansion at 1-year of the ternary blends tested in this program. Referring to Figure 3, increasing the ternary contents has enhanced the resistance. Besides that, the level of reduction in expansion for 15/15, 20/20, and 20%FA+30% Slag is not sufficient to meet the ASTM limit at 1 year (0.1% expansion). However, the 40%FA+20% slag and 20%FA+40%slag mixes have performed well. Yet, 20%FA+40%Slag is the only blend that meets the ASTM limits at 6 month and 1 year.

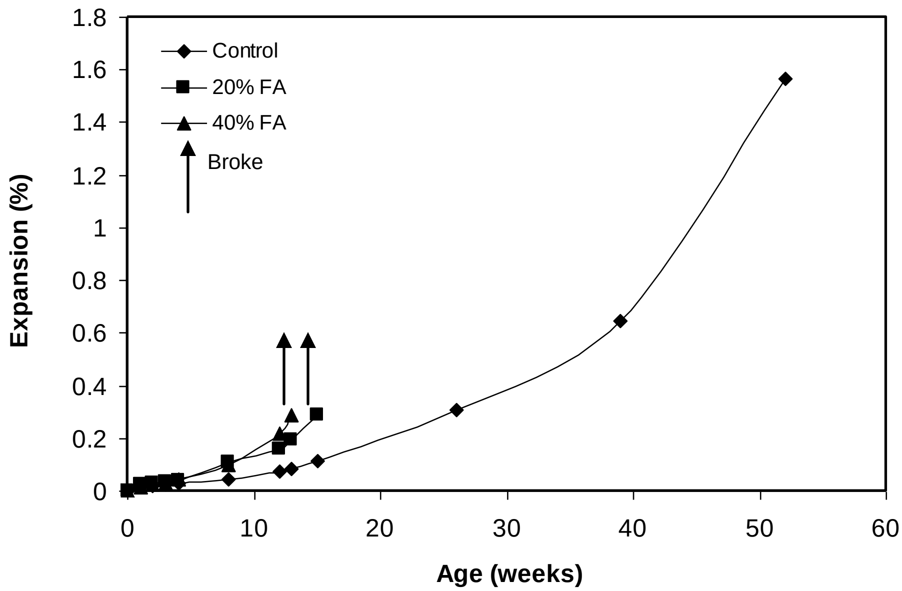

Figure 1: Expansion of Class CH fly ash binary mortar bars in 5% Na_2SO_4 solution

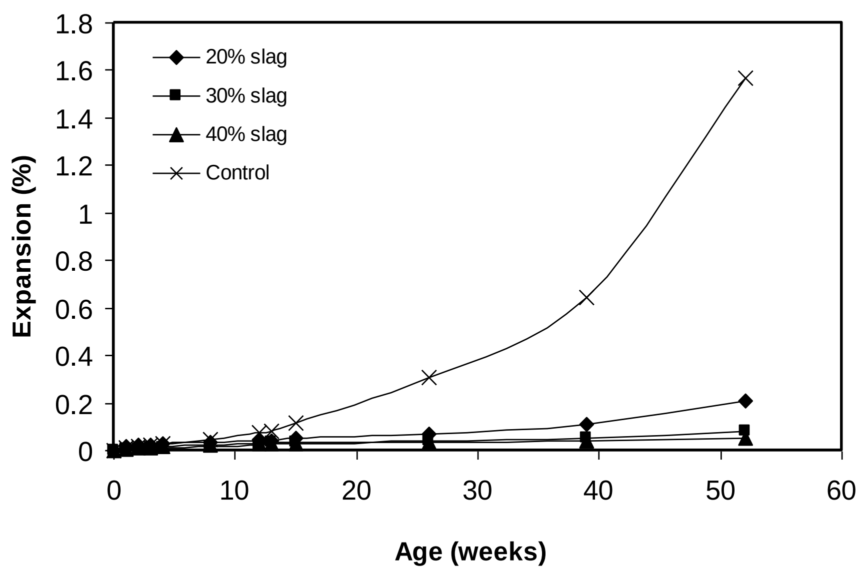

Figure 2: Effect of slag contents on the mortar bar expansion under 5% Na_2SO_4

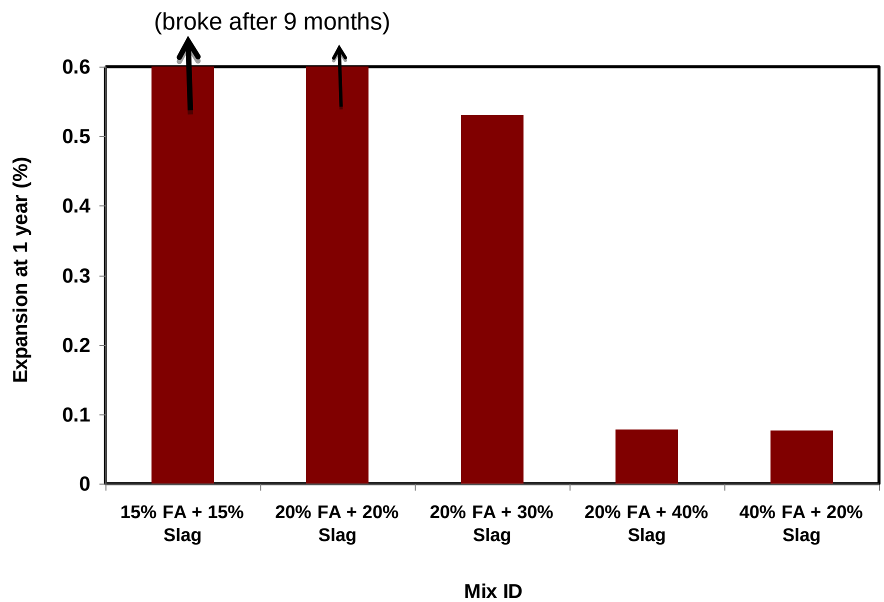

Figure 3: Expansion of ternary blends in Na_2SO_4 solution

5 Discussion

5.1 Effect of Fly Ash Content on the Performance of Ternary Blends

Ternary blends showed promising results that Class CH fly ash could be incorporated in concrete mixes when blended with slag. Figure 4 shows the expansion of ternary blends of 20% slag plus different fly ash contents. Figure 4 illustrates that increasing the fly ash content in ternary blends with slag decreased the expansion. Perhaps this is related, as well, to decreased PC in the mix with high replacement of SCM.

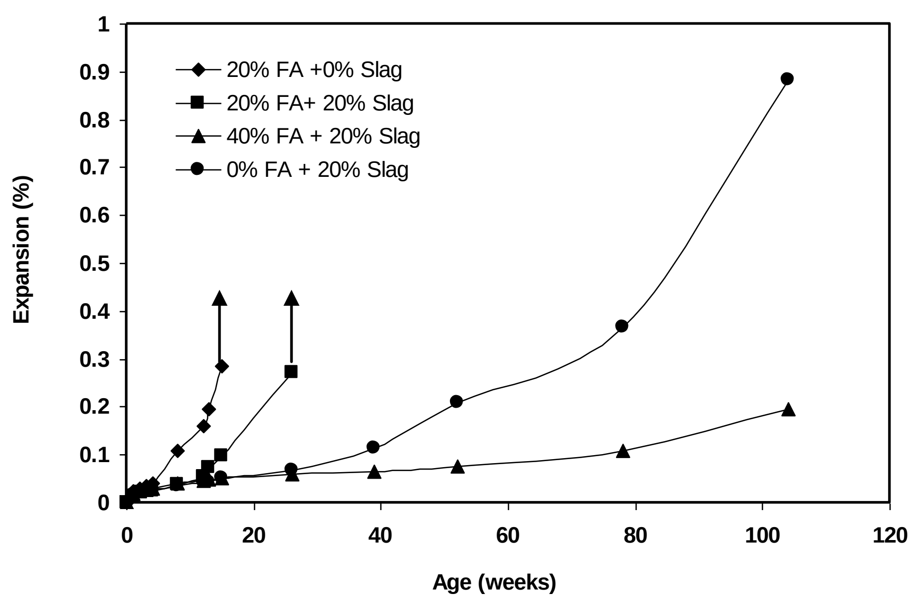

Figure 4: Effect of Class CH fly ash and slag in a ternary system

5.2 Effect of Slag Content on the Performance of Ternary Blends

Figure 5 shows the expansion of ternary blends with 20% fly ash content plus various slag contents. The binary blends of slag are also included in Figure 5 for comparison. The ternary blends reduce the expansion as the slag content increases in the mix. For instance, 20%FA+30%Slag mix resulted in less expansion than 20/20. Similarly, 20%FA+40%Slag resulted in less expansion than 20%FA+30% Slag. It should be noted that adding only 20% slag to 20% HCFA did not produces significant positive effects on the expansion. Higher levels of slag were needed.

Contribution by slag to the performance of ternary blends could be due to several beneficial actions of slag. As a result of pozzolanic reaction, consumption of $Ca(OH)_2$ might have made Ca^{2+} unavailable for ettringite formation. Secondary gel produced due to slag's pozzolanic reaction might have reduced the permeability of the mortar bars. This is evident from the 56^{th} day RCPT values of the mortar mixes which will be shown later in this paper. Increasing slag content resulted in less coulombs passing through the specimens. 20%FA+40%Slag is less permeable (2722 Coulombs) than 20%FA+30%Slag (3258 C) and 20%FA+30%Slag is more permeable than 20/20 (4017 C). In addition, slag results in lower Ca/Si ratio of C-S-H which could make more Al^{3+} to be incorporated into C-S-H, thus making Al^{3+} not available for ettringite formation (Gollop and Taylor, 1996).

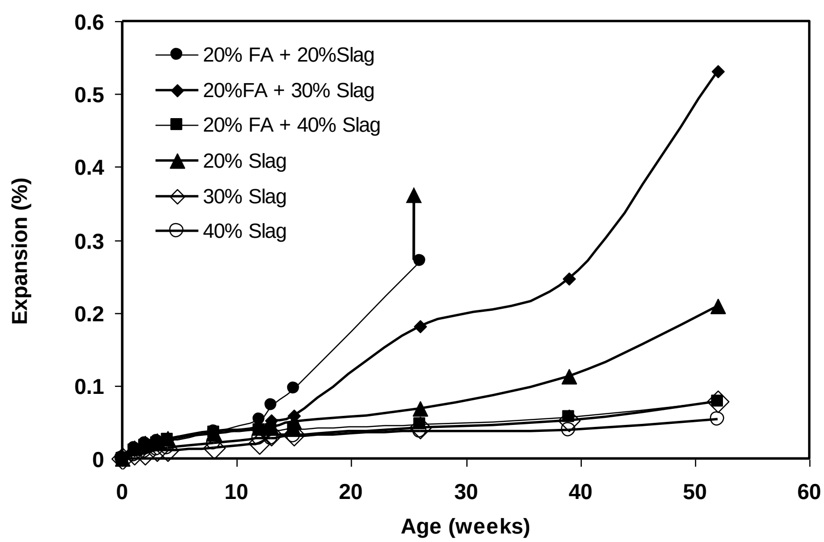

Figure 5: Effect of slag content on expansion of ternary blends

5.3 Calcium Hydroxide Contents

Figure 6 shows the relationship between the mortar bar expansion and the $Ca(OH)_2$ content of paste samples. Note that the fly ash mixes are not included as the fly ash binary blends disintegrated before 6 months.

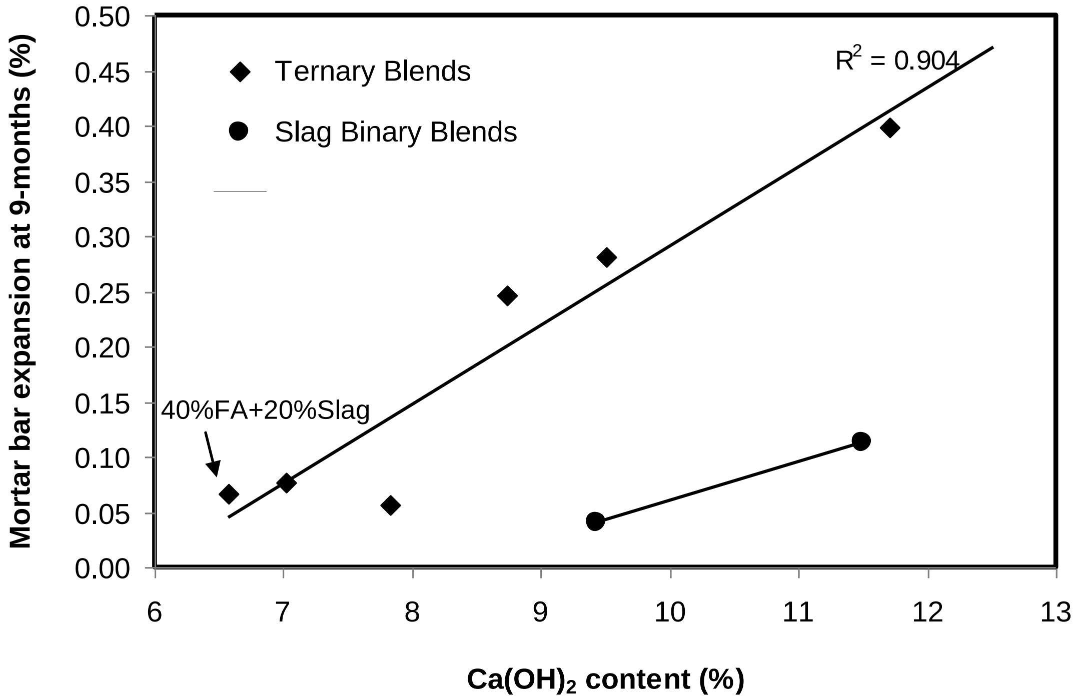

Figure 6: Relationship between mortar bar expansion of $Ca(OH)_2$ content of the paste

The calcium hydroxide contents of the blends with SCM are lower than that of the control. Control paste with only Portland cement contained 19.2% $Ca(OH)_2$ where adding 20% FA have reduced the $Ca(OH)_2$ to 11.5%. In addition, Figure 6 shows the relationship between the $Ca(OH)_2$ and the mortar bar expansion of ternary blends with R^2 of 0.904. The obtained correlation confirms that $Ca(OH)_2$ consumption is a contributing factor for the performance of ternary blends. Out of all the ternary blends tested, 40%FA+20% Slag blend resulted in lowest $Ca(OH)_2$ content. This confirms that increased $Ca(OH)_2$ consumption of 40%FA+20Slag is a contributing factor for the excellent performance of this blend. Further, the blends 30+30, and 20%FA+40%Slag also obtained lower $Ca(OH)_2$ contents, confirming that increased $Ca(OH)_2$ consumption is a contributing factor for the reduced expansion of the mortar bars of these blends. It is clear that for the same $Ca(OH)_2$ content samples with only slag showed lower expansion that samples containing both fly ash and slag. This is due to the negative effects of fly ash on sulphate resistance or, in other words, the presence of sulphate–vulnerable phases in the HCFA, namely calcium aluminates (Shehata et al., 2008).

5.4 Ion Diffusivity

Rapid Chloride Permeability test (RCPT) values of mortar specimens at 56 days are given in Table 3. The values on Table 3 are average of at least two specimens. Lower permeability will limit the sulphate ions migration into the concrete/mortar hence improve the resistance. Lower ion diffusivity also indicates increased hydration level or more C-S-H which might incorporate more reactive alumina in it (Shehata et al., 2008).

Table 3: RCPT test results of the blends tested for sulphate attack

Mix ID	**Total Charges Passed during RCPT at 56^{th} day (Coulombs)** * indicates OVF states before RCPT finished; predicted value at the time of OVF is given
Control (100% PC1)	6627
20% FA	6988
40 FA	9360*
20 Slag	5209
30 Slag	3874
40 Slag	2689
20%FA +20%Slag	4017
20 FA+30 Slag	3258
15 FA+15 Slag	4966
40 FA+20 Slag	7958
20 FA+40 Slag	2722
30 FA+30 Slag	5073

The RCPT values at 56 days are plotted against the mortar bar expansion at 9 months and shown in Figure 7. Two different trends were observed between mortar bar expansion and 56-day RCPT, namely Group 1 and Group 2. The 20%FA+40%Slag, and 40% slag blends are included in both Groups since they are located in the path of the both of them.

The expansion of blends located in group-1 is influenced by permeability to a considerable degree. The blends of group-2 cannot be explained based on permeability. For instance, 20%FA+40%Slag and 40%FA+20%Slag have a huge difference in their permeability but the expansion values are very close to each other.

The permeability trend in Figure 7 does not provide a ground to explain the lower 9-month expansion of 30/30 and 40%FA+20%Slag. This pattern reveals that the blends in Group 2 are mainly affected by other factors that influence sulphate attack. Earlier it was showed that 40%FA+20%Slag blend was the one that consumed more $Ca(OH)_2$ than any other blends tested. 30/30 was the one with second most consumption of $Ca(OH)_2$. Though the blends, 40%FA+20%Slag and 30/30 had higher permeability, their lower mortar bar expansion could be explained based on their higher consumption of $Ca(OH)_2$.

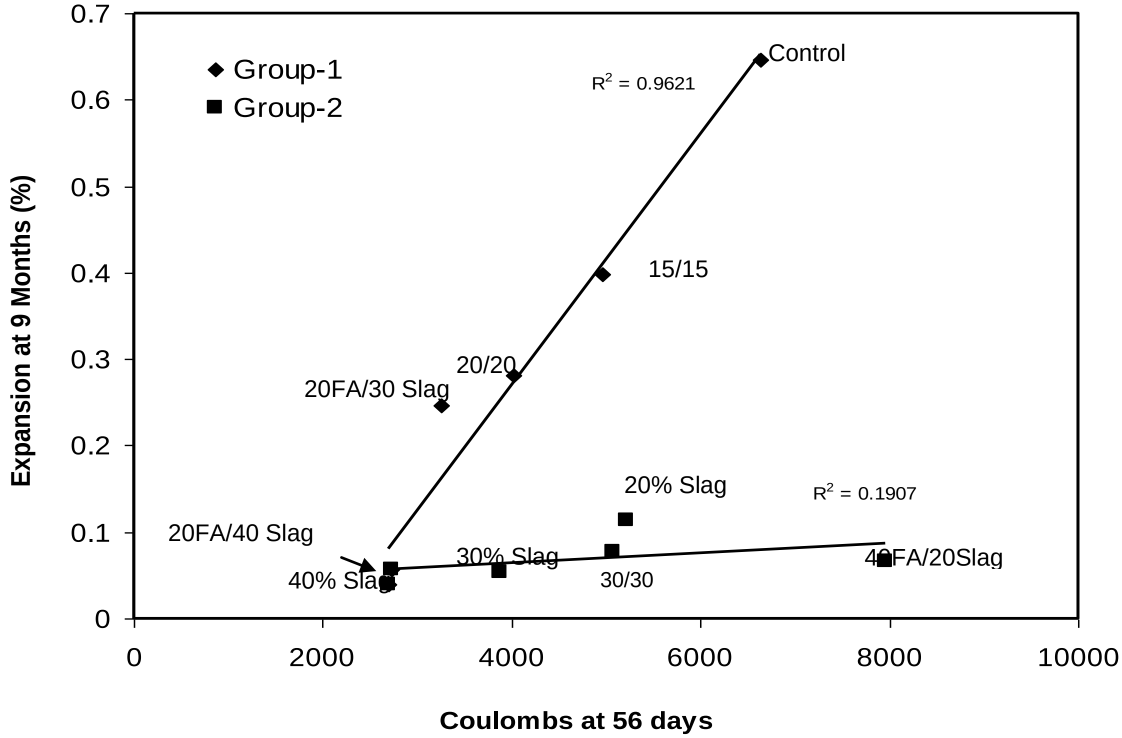

Figure 7: Correlation between mortar bar expansion and RCPT at 56th day

6 Conclusion

For the materials investigated in this study, the following conclusions are drawn:

1. Adding slag to HCFA reduced the expansion due to sulphate attack.
2. The incorporation of slag as little as 20% into the blend made possible to incorporate Class CH fly ash with increased resistance.
3. The ternary blend with 40% Class CH fly ash + 20% slag resulted in superior performance knowing that 40% Class CH fly ash binary blend dramatically reduced the resistance. This is attributable to the consumption of calcium hydroxide and reduced ion diffusivity.
4. Enhanced resistance to sulphate attack could not be explained based solely on the reduced ion diffusion through the mix. It is believed that incorporation of reactive alumina in hydration products, and calcium consumption are among other factors controlling sulphate resistance.

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