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Redefining cement characteristics for sulfate-resistant Portland cement

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Abstract

Experimental research was performed to relate specific cement characteristics to expansion due to sulfate attack. Twenty-one North American cement of statistically diverse chemical composition were used in the study. ASTM 1012 "Standard Test Method for Length Change of Hydraulic Cement Mortars Exposed to a Sulfate Solution" was performed using mortars prepared with each of the cement. First-order and multivariate relationships between cement characteristics and sulfate expansion were correlated at different ages. Analysis revealed that while tricalcium aluminate (C_3A) has typically been targeted as the chief contributor to sulfate attack, iron oxide (Fe_2O_3) or tetracalcium aluminoferrite (C_4AF) content, combined with total equivalent alkalis, showed a much stronger negative correlation with expansions at all ages. These results are in agreement with a broad spectrum of sulfate expansion theories and can provide a better means of specifying sulfate-resistant cement. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Cement; Sulfate attack; Concrete; Modeling

1. Introduction

Sulfate attack causes deterioration in concrete structures exposed to moist, sulfate-rich environments. The resistance to sulfate attack has long been known to be connected to the characteristics of the cementitious material [1–4]; however, the complex reactions in hydrating cement have made it difficult to isolate more than one variable at a time. The statistical relationship of multiple cement characteristics to sulfate attack is the subject of this research. The research study performed sulfate resistance testing on mortar specimens prepared from 21 types of cement with statistically broad chemical and physical characteristics, and developed multivariate model relationships between these characteristics and the results of sulfate resistance testing using Na_2SO_4 as the aggressive medium.

2. Sulfate resistance

Sulfate attack typically occurs in structures exposed to solutions high in sulfates, such as seawaters, rivers, or some groundwater. Upon the penetration of sulfate ions into the concrete, the calcium monosulfoaluminate crystals in the paste may convert into gypsum or ettringite; this results in a change to a larger molar volume. These volumetric changes cause expansion and internal stresses, which ultimately weaken and destroy the paste bonds, deteriorating the concrete. Surface layers are particularly affected and are subject to a high level of spalling, which increases the exposure conditions for interior concrete.

There is a large volume of literature on the theoretical mechanisms of sulfate attack, combined with experimental evaluations [2,5–7]. All these studies mainly relate C_3A content of the cement and the concentration of sulfates in the exposure solution to the external sulfate attack. Roy [7] gives the chemical reactions occurring in sulfate attack. The reactions form ettringite, gypsum, or brucite, shown schematically as follows:

1. Ettringite formation

$$4CaO \cdot Al_2O_3 \cdot xH_2O + 3CaSO_4 \cdot 2H_2O + H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + Ca(OH)_2$$

2. Gypsum, ettringite, and brucite formation

$$Ca(OH)_2 + MgSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + Mg(OH)_2$$

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$$3CaO \cdot Al_2O_3 \cdot 6H_2O + 3CaSO_4 \cdot 2H_2O + H_2O$$
$$\rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$$

Both sodium and magnesium sulfates contribute to sulfate attack, with their effectiveness regulated by the presence of other ions in solution. Solutions containing magnesium sulfate have been shown to be more detrimental than solutions containing the same concentration of sodium sulfate because both SO_4^{2-} and Mg^{2+} contribute to the damage. The absence of calcium hydroxide ($Ca(OH)_2$) increases magnesium sulfate attack [6]. Hewlett [2] states that sodium sulfate solutions have a more pronounced effect on cement with high C_3A contents, while magnesium sufate solution has a more pronounced effect on cement of lower C_3A content. Cohen and Bentur [12] confirmed these results with research on the effects on sulfate attack of sodium, potassium, magnesium, and calcium cations in solution.

A high level of sulfate attack has historically been attributed to a high C_3A content in Portland cement and a high SO_3 content in the environment. The largest study conducted on cement showed that cement with C_3A contents above 12% performs poorly, while cement with contents below 9% usually performs satisfactorily [10]. Cement between the two values shows a wide range of performance. This disparity can partly be explained because cement with a higher Bogue C_3A content has a significantly different effect than cement with high crystalline C_3A [9]. Aluminates (Al_2O_3) present in unreacted C_3A react with the sulfates, initiating the primary expansion mechanism. Although the expansive reactions are ultimately limited by the amount of Al_2O_3 present, the presence of CaO and SO_4 is also necessary for the crystalline transformation to proceed [2].

The role of C–S–H on sulfate attack is well documented. According to Mehta [8] and Skalny and Pierce [18], studies on the ettringite expansion phenomenon alone are inadequate to explain the sulfate attack on Portland cement concrete. Physico-chemical effects of sulfate ions on all the phases of the hydrated cement paste must be considered. Rasheeduzzafar et al. [6] cite the following reasons for the increase in sulfate attack due to C_3S/C_2S ratio and quantity of $Ca(OH)_2$ produced in the cement hydration.

(1) The solubility of expansive hydrated calcium aluminates is lowered significantly in a saturated lime environment, thereby making the sulfate reaction topochemical and expansive in nature (Refs. [1,19] indicate that these reactions are not topochemical).

(2) In high hydroxyl concentration contributed by a rich $Ca(OH)_2$ environment, ettringite formed is microcrystalline, which is capable of adsorbing large amounts of water on the surface, and causing considerable disruptive expansion.

(3) Enhanced $Ca(OH)_2$ results in increased gypsum formation, causing reduction in strength and stiffness of concrete.

Another of the keys to sulfate resistance is permeability, which is linked to porosity. A more refined paste structure, with a dense interlocking network of C–S–H crystals, will improve resistance to sulfate attack by reducing the ability of the ions to diffuse into the concrete. It has been shown that even cement with high C_3A content can show sulfate resistance if they are impermeable enough [7]. Chemical components in the cement that control permeability, such as the C_3S/C_2S ratio, help to control the rate and severity of sulfate attack. Cement with high C_3S/C_2S ratios are prone to sulfate attack [11] because of the higher amount of $Ca(OH)_2$ produced during hydration.

Substitution of C_4AF for C_3A has resulted in decreased susceptibility to sulfate attack [2]. This discovery led to the development of sulfate resistance cement. However, too much C_4AF can decrease the sulfate resistance of low C_3A cement [1]. In the largest study conducted on sulfate resistance, Blaine and Arni [10] showed results that prominently displayed C_3A as a dominant factor in sulfate expansion. The relationship between cement with low C_3A contents (0–7%) and expansion is linear, but exponential relationships of the second or third degree seem to best express the relationship between high C_3A cement (7–15%) and expansion. The results of Blaine and Arni show that cement characteristics affect the expansions of high C_3A cement and low C_3A cement differently. For high C_3A cement, the principal variables in sulfate expansion, other than C_3A, were Fe_2O_3 and the CaO/SiO_2 ratio. A high Fe_2O_3 content and/or a high CaO/SiO_2 ratio resulted in lower expansion at all durations of the test. For low C_3A cement, loss on ignition, insoluble residue, and K_2O content were associated with higher expansions. However, the effects of these characteristics became less evident over time.

Blaine and Arni [10] showed that several trace elements seemed to have minor effects on sulfate attack. Strontium (Sr), chromium (Cr), nickel (Ni), phosphorus (P), vanadium (V), and zinc (Zn) all had a slight positive correlation with sulfate expansion, while copper (Cu) had a slight negative correlation. The work of Blaine and Arni [10] also looked at the relationship of compressive strength of mortar cubes to the sulfate expansion results. A negative correlation seemed to indicate that a high tricalcium silicate (C_3S) content, which results in high early mortar strength, led to decreased expansion levels. Skalny and Pierce [18] indicated that there were still many questions concerning the complex characteristics of modern cement, and their effects on sulfate attack. Brown and Taylor [19] have emphasized that, beyond the chemical effects, there are many unresolved questions con-

Table 1
Target values for selected cement characteristics

	SO_3 (%)	Equivalent alkalis (%)	C_3A (%)	Fineness (Blaine)
Extremely high	4.2	1.1	15	4600
High	3.6	0.85	12	4200
Average	3	0.6	9	3800
Low	2.4	0.35	6	3400
Extremely low	1.8	0.1	3	3000

Table 2
Chemical characteristics of Portland cement in the study

Code	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI	Na_2O	K_2O	TiO_2	P_2O_5	ZnO	Mn_2O_3	B_2O_3	BaO	Cr_2O_3	NiO	SrO	Cl
1	20.91	3.97	2.99	62.97	3.27	2.83	1.46	0.10	0.45	0.21	0.03	0.105	0.134	0.030	0.046	0.012	0.011	0.147	< 0.001
2	21.45	4.01	4.02	64.65	1.39	2.38	0.59	0.20	0.49	0.25	0.16	0.018	0.067	0.015	0.018	0.028	0.016	0.090	0.001
3	20.26	4.45	3.20	63.81	1.55	4.13	1.52	0.16	0.46	0.23	0.04	0.022	0.420	0.020	0.022	0.155	0.010	0.054	< 0.001
4	19.79	5.46	1.61	64.49	1.16	3.77	1.64	0.15	0.92	0.28	0.11	0.014	0.052	0.021	0.020	0.016	0.011	0.106	0.005
5	20.56	5.02	1.94	63.77	3.77	2.73	1.23	0.09	0.56	0.34	0.19	0.024	0.095	0.016	0.025	0.018	0.014	0.328	< 0.001
6	20.45	5.61	2.90	63.94	1.88	3.00	1.02	0.18	0.12	0.55	0.07	0.024	0.078	0.062	0.045	0.032	0.020	0.108	0.001
7	19.81	6.03	2.54	64.46	0.88	3.04	1.37	0.24	0.39	0.63	0.21	0.032	0.061	0.015	0.041	0.018	0.009	0.300	< 0.001
8	20.08	5.47	2.90	63.77	1.15	3.13	2.11	0.12	0.79	0.29	0.12	0.017	0.156	0.012	0.068	0.011	0.007	0.178	0.008
9	20.49	5.14	2.54	63.10	1.74	3.84	1.41	0.18	1.00	0.30	0.11	0.018	0.151	0.014	0.021	0.010	0.007	0.121	0.002
10	21.12	4.42	2.48	63.89	1.99	2.81	1.44	0.47	0.67	0.24	0.16	0.012	0.048	0.010	0.034	0.012	0.017	0.198	0.001
11	19.61	5.25	2.60	62.43	2.11	4.35	1.71	0.20	1.09	0.25	0.08	0.040	0.090	0.017	0.016	0.025	0.010	0.108	0.003
12	20.54	4.56	3.18	61.01	5.01	3.48	1.12	0.25	0.82	0.26	0.05	0.011	0.101	0.018	0.033	0.011	0.007	0.076	< 0.001
13	21.33	4.04	2.88	63.85	1.25	2.68	1.52	0.13	0.36	0.18	0.20	0.017	0.240	0.019	0.044	0.010	0.009	0.230	0.002
14	21.08	4.70	3.12	63.96	1.22	2.68	1.46	0.10	0.61	0.20	0.09	0.013	0.069	0.009	0.026	0.020	0.007	0.050	0.003
15	20.20	4.58	2.59	62.65	2.09	3.26	1.74	0.20	0.93	0.23	0.18	0.041	0.092	0.022	0.016	0.025	0.008	0.113	0.006
16	20.77	4.55	1.52	63.71	2.48	3.05	1.46	0.06	0.02	0.36	0.15	0.040	0.156	0.022	0.021	0.029	0.009	0.040	0.002
17	21.25	4.29	2.44	63.37	2.04	3.19	0.84	0.39	0.71	0.27	0.18	0.017	0.116	0.017	0.024	0.029	0.011	0.250	0.002
18	19.72	5.27	1.97	63.14	3.27	3.43	0.73	0.32	1.15	0.22	0.23	< 0.005	0.063	0.028	0.020	0.010	0.006	0.320	0.011
19	20.29	5.54	2.90	64.97	1.04	2.73	0.70	0.11	0.83	0.28	0.17	0.006	0.143	0.021	0.048	0.010	< 0.005	0.144	< 0.002
20	20.68	4.84	3.23	64.65	1.85	2.90	0.70	0.04	0.54	0.30	0.07	< 0.005	0.024	0.019	0.022	< 0.005	< 0.005	0.050	< 0.002
21	20.40	4.63	2.91	61.76	3.96	3.18	1.36	0.32	0.57	0.28	0.10	0.010	0.041	0.018	0.021	0.016	< 0.005	0.098	< 0.002

cerning damage related to ettringite expansion through reaction of external sulfates with concrete and the various hypotheses that have been forwarded to explain the destruction expansion.

Despite all the research in this area, a working predictive model does not exist. While AASHTO M85 and ASTM C150 use C_3A as a linear predictive measure, this is not the observed behavior in any scientific study, but rather a convenient manner of specifying cement with a single variable.

3. Methods and materials

The study reported herein evaluated the effect of cement characteristics on sulfate resistance. Twenty-one types of

Table 3
Physical and chemical characteristics of Portland cement in the study

Bogue chemical composition (% by mass)					BET surface area (m^2/g)	Blaine fineness (m^2/kg)	Wet sieve analysis ASTM C430 (% by mass)	Normal consistency ASTM C187 (% by mass)	Isothermal calorimetry (24 h) (kJ/kg)	Heat of hydration ASTM C186(kJ/kg)		
Code	C_3S	C_2S	C_3A	C_4AF						7 days	14 days	28 days
1	58.4	15.9	5.5	9.1	1.83	4084	94.11	24.5	180	341	418	431
2	60.7	15.7	3.8	12.2	1.05	3622	93.66	24.5	65	289	293	418
3	59.5	13.2	6.4	9.7	1.73	4048	97.32	25.5	180	257	344	347
4	62.4	9.7	11.7	4.9	1.48	3282	89.95	24.7	172	355	367	380
5	59.1	14.4	10.0	5.9	1.44	3871	89.81	24.3	168	392	475	468
6	54.5	17.5	10.0	8.8	1.32	3831	94.36	25.0	160	209	455	456
7	59.0	12.2	11.7	7.7	1.80	3705	96.30	25.7	178	429	479	523
8	57.2	14.4	9.6	8.8	1.82	4009	91.28	25.0	198	334	385	451
9	52.0	19.5	9.3	7.7	1.54	3871	89.03	25.0	151	287	380	497
10	58.3	16.5	7.5	7.5	1.41	4345	95.97	25.0	213	403	478	497
11	53.7	15.7	9.5	7.9	1.42	4029	92.67	24.5	176	428	581	598
12	47.2	23.3	6.7	9.7	1.50	3950	96.88	25.7	150	222	226	234
13	58.9	16.7	5.8	8.8	1.54	3768	95.60	25.0	171	311	401	485
14	56.5	17.8	7.2	9.5	1.36	3600	97.13	25.1	169	348	362	410
15	57.8	14.3	7.8	7.9	1.47	4179	91.80	25.3	196	468	502	535
16	60.1	14.2	9.5	4.6	1.59	3850	94.71	24.9	217	357	362	***
17	55.1	19.4	7.2	7.4	1.17	3384	95.82	24.6	157	321	394	431
18	59.2	11.9	10.6	6.0	1.03	3663	95.21	26.8	165	301	456	426
19	61.1	12.0	9.8	8.8	1.07	3803	89.25	24.6	172	314	385	497
20	60.6	13.6	7.4	9.8	1.05	3930	95.67	25.2	176	322	401	435
21	52.0	19.2	7.3	8.9	1.37	4104	95.56	27.0	173	322	460	481

*** data not available.

Table 4
Sulfate attack expansion at various exposures by ASTM C1012 test

Cement number	SO_3	Alkalies	C_3A	C_4AF	Sulfate expansion (%) 2 weeks	1 month	2 months	13 weeks	4 months	6 months
1	2.83	0.39	5.5	9.1	0.022	0.035	0.053	0.075	0.102	0.178
2	2.38	0.52	3.8	12.2	0.015	0.023	0.030	0.043	0.051	0.090
3	4.13	0.46	6.4	9.7	0.017	0.025	0.043	0.071	0.101	0.233
4	3.77	0.76	11.7	4.9	0.019	0.033	0.082	0.345	0.745	2.052
5	2.73	0.46	10.0	5.9	0.019	0.031	0.067	0.298	0.708	1.981
6	3.00	0.26	10.0	8.8	0.011	0.020	0.038	0.106	0.230	0.595
7	3.04	0.50	11.7	7.7	0.007	0.012	0.024	0.070	0.210	0.873
8	3.13	0.64	9.6	8.8	0.012	0.020	0.035	0.058	0.083	0.272
9	3.84	0.84	9.3	7.7	0.014	0.020	0.030	0.044	0.055	0.093
10	2.81	0.91	7.5	7.5	0.016	0.021	0.034	0.065	0.111	0.363
11	4.35	0.92	9.5	7.9	0.019	0.051	0.042	0.087	0.152	0.397
12	3.48	0.79	6.7	9.7	0.013	0.024	0.031	0.051	0.060	0.092
13	2.68	0.37	5.8	8.8	0.008	0.015	0.039	0.065	0.125	0.387
14	2.68	0.50	7.2	9.5	0.018	0.024	0.098	0.145	0.233	0.742
15	3.26	0.81	7.8	7.9	0.017	0.025	0.046	0.189	0.308	0.878
16	3.05	0.07	9.5	4.6	0.012	0.028	0.066	0.324	0.698	1.582
17	3.19	0.86	7.2	7.4	0.010	0.016	0.038	0.068	0.130	0.364
18	3.43	1.00	10.6	6.0	0.011	0.020	0.054	0.195	0.317	1.297
19	2.73	0.66	9.8	8.8	0.014	0.020	0.027	0.079	0.179	0.702
20	2.90	0.39	7.4	9.8	0.019	0.025	0.030	0.054	0.209	0.146
21	3.180	0.700	7.3	8.9	0.013	0.015	0.033	0.059	0.073	0.135

cement with varying chemical components were used to model the wide range of compositions of Portland cement. A survey of North American cement was conducted with the assistance of the Portland Cement Association. All the chemical and physical characteristics on a standard mill analysis were studied to determine the variation in properties in Portland cement. A statistical analysis model was developed using these data. Extreme low, low, mean, high, and extreme high values of four characteristics were chosen from this analysis: SO_3 content, C_3A content, alkali content, and fineness. These values are displayed in Table 1.

Using these values as guidelines, AASHTO M85 Types I and II cement were selected from a coded manufacturer inventory sheet. Five "average" cement types were selected in order to form the center points of the statistical matrix. Eight cement types were selected as "corner points" for the model to represent high- and low-value combinations for the characteristics of interest. Another eight cement types were selected as "star points" representing the extreme high and low values for each of the four characteristics. The chemical characteristics and other properties of the selected cement, as determined by laboratory testing, are listed in Tables 2 and 3. It is not possible to match each target with production cement as some combinations do not exist for performance reasons, e.g., high C_3A and low SO_3.

Mortar mixtures were prepared according to ASTM C1012, "Standard Test Method for Length Change of Hydraulic Cement Mortars Exposed to a Sulfate Solution." For each cement, between six and eight mortar bars were immersed in 50 g/l sodium sulfate (Na_2SO_4) solution. Comparator readings were taken at 1, 2, 3, 4, 8, 13, and 15 weeks, and at 4, 6, 9, and 12 months. Measurements were made using a length comparator according to ASTM C157 and mortar cubes (51 mm) were made using the same mortar. Half of the cubes was immersed in the sodium sulfate solution, while the others were cured in a lime bath. These cubes were evaluated for strength according to ASTM C109.

4. Statistical analysis

Data compiled during this study were cataloged and analyzed using several computer software programs. Raw data were entered in a formatted database and subsequently analyzed for pertinent properties and trends. This required

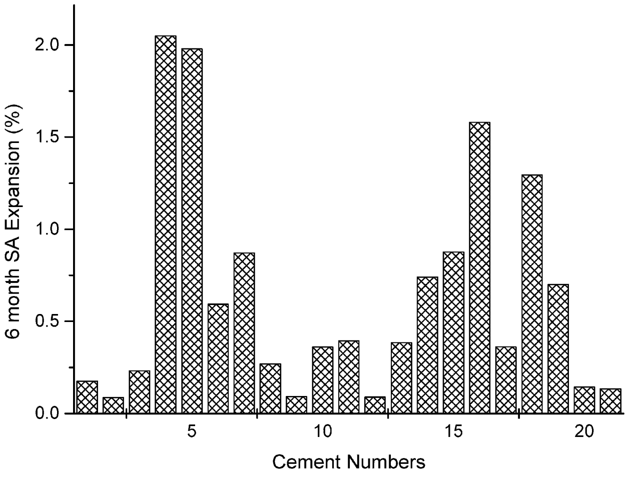

Fig. 1. Six-month expansion of mortar bars in ASTM C1012 test.

Table 5
Single variable statistical analysis for sulfate attack, 4 months

Cement characteristic	R^2	P value
Fe_2O_3	.773	.000
C_4AF	.745	.000
C_3A	.460	.031
C_2S	.307	.037
C_3S	.254	.072
SrO	.242	.083
Total equivalent alkalis	.180	.168
TiO_2	.164	.199
Na_2O	.155	.220
K_2O	.148	.237
Blaine fineness	.138	.264
Al_2O_3	.119	.318
P_2O_5	.087	.440
ZnO	.083	.459
CaO	.082	.464
BaO	.081	.469
NiO	.077	.485
BET surface area	.076	.491
Cr_2O_3	.073	.504
SiO_2	.063	.557
B_2O_3	.060	.575
Cl	.057	.590
MgO	.034	.730
SO_3	.031	.750
Mn_2O_3	.029	.771

computation of the percent expansion for each specimen and then averaging for the total number of specimens for each cement.

After raw data were compiled into useful formats, they were inserted into the database with the cement characterization data. A series of plots was made using one independent variable (cement characteristic) and one dependent variable (experimental result). Visual inspection of these plots, when combined with statistical analysis results, allowed for first-order relationships between cement characteristics and expansion to be further understood.

For each independent and dependent variable, several types of statistical analysis were performed using a statistical software program. Correlation coefficients and corresponding P values were computed and recorded. Linear r^2 values were computed by squaring the correlation coefficients. Linear regression was then performed using quadratic analysis. The r^2 and P values were again recorded. Comparison of the r^2 values for the linear and quadratic regression analysis revealed the best fit to the data. In order to establish a criterion for further evaluation, only r^2 values greater than .4 were considered to have significant first-order correlation. The regression equations for significant relationships were subsequently recorded.

5. Results

Expansion rates varied significantly for each cement in the study. Table 4 shows the expansion values through 6 months. The 12-month data were not useful in modeling statistical behavior because more than half of the cement had expanded to fracture. These data are statistically invalid for mathematical modeling. The distribution of 6-month expansions is shown in Fig. 1. Note that the expansions relate an approximate uniform distribution from highly expansive cement to nearly zero expansion, as desired by the initial experimental model. In the particular environment of the C1012 test, only the data beyond 4 months were useful in predicting behavior in the C1012 test results. Statistical analysis was performed on the early age data,

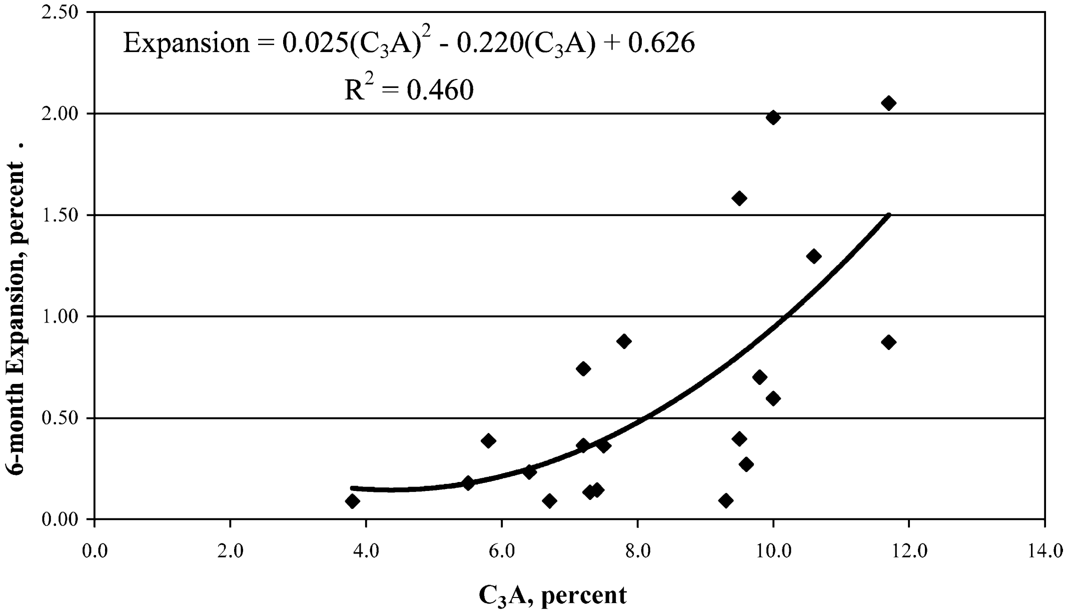

Fig. 2. Correlation between C_3A and sulfate expansions.

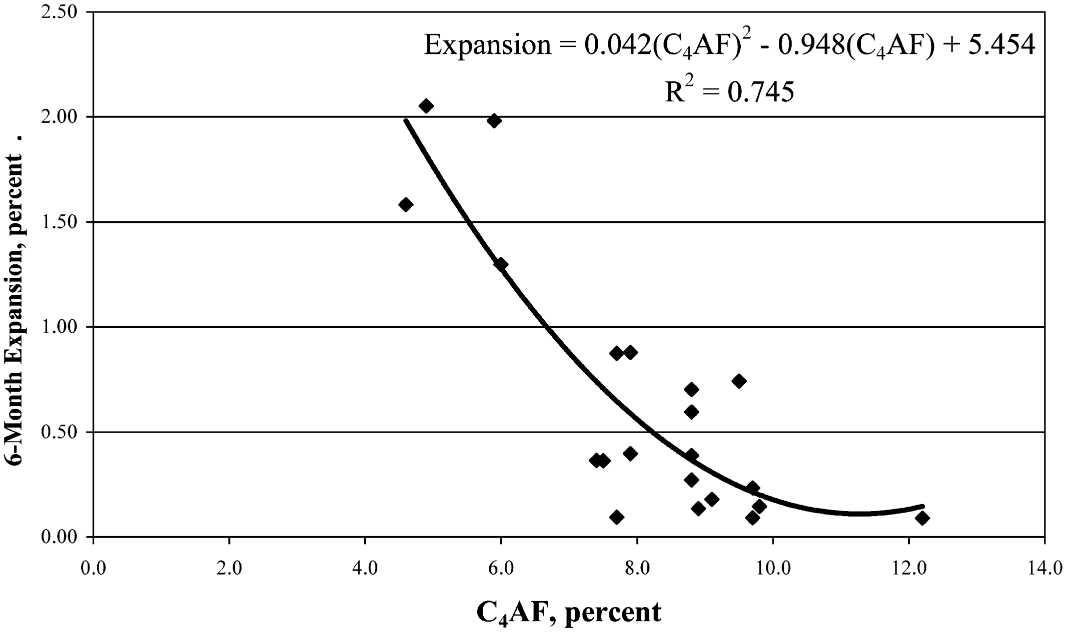

Fig. 3. Correlation between C_4AF and sulfate expansions.

but no significant correlations were found. While data were collected through the 1-year date, the 9-month and 1-year data did not have predictive value because some specimens had fractured, leaving them without quantitative expansion data associated with time for statistical correlation. However, after 4 months, it was clear that Fe_2O_3 and C_4AF content showed very strong negative correlations with sulfate expansion, as shown in Table 5. The R^2 values of .773 and .745, for Fe_2O_3 and C_4AF, respectively, eclipse the values of all other chemical characteristics, which had R^2 values less than .500 (C_3A had a positive correlation, with an R^2 of .460). The individual correlations at 6 months were nearly the same as the 4-month correlations. Figs. 2 and 3 show the single variable correlations with C_3A (positive) and C_4AF (negative), respectively.

The research study looked to improve on the correlation using multivariate analysis using the 6-month expansion data. Multivariate analysis of potential predictive variables was performed after 6 months using a commercially available statistical software package. The 6-month expansions were evaluated for all first- and second-order effects. The most relevant variables were combined to evaluate potential third-order correlations. Using polynomial equations, Fe_2O_3, C_4AF, C_3A, total equivalent alkalies, K_2O, Na_2O, Al_2O_3,

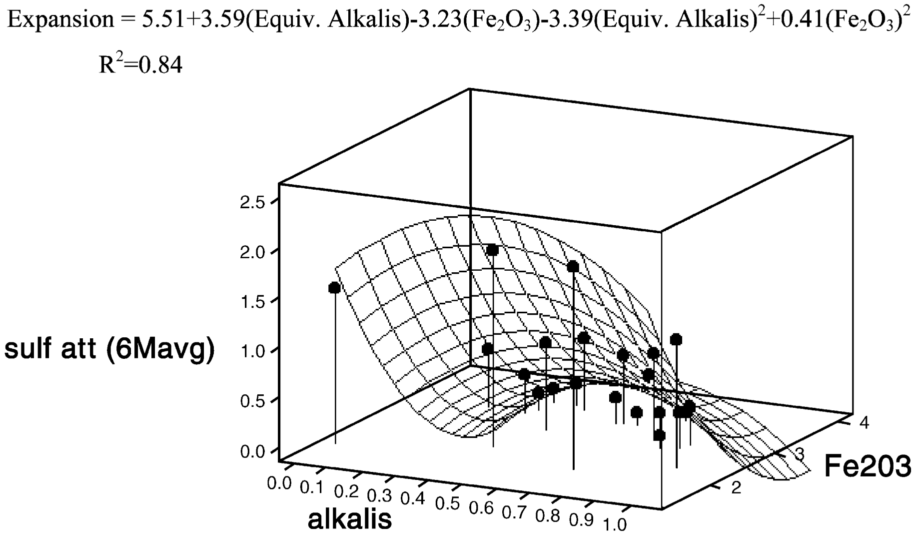

Fig. 4. Multivariate relationship among Fe_2O_3, alkalis, and percent sulfate expansion.

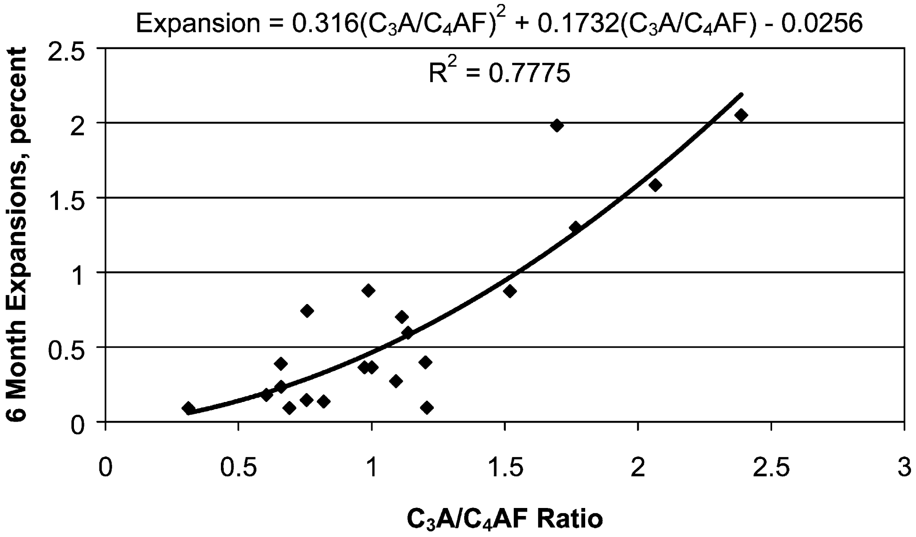

Fig. 5. Multivariate relationship among C_3A, C_4AF, and sulfate expansions.

C_3S/C_2S, C_3A/C_4AF, and SrO were correlated with sulfate expansions. In nearly every case, equations containing Fe_2O_3 or C_4AF were the best predictive equations. The most accurate predictions came from the use of Fe_2O_3 and total alkalies. The relationship among Fe_2O_3, alkalies, and expansion is shown in Fig. 4. The R^2 value of .84 is very good for an empirical relationship and is substantially better than any predictive equation containing C_3A. The best predictive equation containing C_3A involved the relationship containing the C_3A/C_4AF ratio, with an R^2 value of .78, shown in Fig. 5. This correlation is only slightly improved over C_4AF alone (Fig. 3).

6. Discussion

The C_3A content of Portland cement has long been assumed to be the chief contributor to volume change in sulfate attack [3,10]. It is interesting to note that C_3A alone showed no significant correlation with sulfate expansions at any age. In this study, Fe_2O_3 was clearly the most predictive variable in sulfate resistance. This result is not in conflict with Blaine and Arni [10], as they found that for C_3A contents greater than 9%, one of the other principal controlling cement characteristics is Fe_2O_3 content. In addition to Fe_2O_3 content, with only slightly lower r^2 values, the related variable C_4AF also showed as a dominant factor. Combined, these data point to the strong influence of iron in this reaction. Substitution of C_4AF for C_3A has been shown to reduce susceptibility to sulfate attack, although it has also been shown that too much C_4AF can decrease the resistance of low C_3A cement [2]. Clearly, no correlation was found between SO_3 content and the cement and the sulfate attack expansion in this study because none of the cement was over- or undersulfonated, but rather optimized to balance the C_3A.

Resistance of many cement not susceptible to sulfate attack has been attributed to a lower amount of C_3A in the clinker. In fact, ferrite is the major oxide interstitial phase in sulfate-resisting Portland cement [13]. However, in order to achieve this, the Al_2O_3/Fe_2O_3 ratio in C_4AF is decreased by the addition of iron, which in turn raises the C_4AF content. Odler and Jawed [14] explain that C_4AF also produces ettringite, but at a reaction rate much slower than C_3A, and the resulting ettringite crystals contain iron along with aluminum in the lattice. Odler and Jawed relate that the iron-containing ettringite phases are much less expansive than iron-free phases, although the reason is not quite understood. This lower expansion may be either due to the differences in crystal morphology, or the fact that the slower rate of formation of the iron-containing phases allows the cement paste structure to be strong enough to resist the expansive stresses [14,15]. Odler and Gasser [15] observed through scanning electron microscopy (SEM) examination that the iron-free ettringite phases had distinct acicular crystals, while the iron-containing phases had a less needle-like morphology. Additionally, Odler and Gasser noted an absence of any distinct ettringite crystals in a paste made from a high-iron clinker, which supports the existence of a different morphology between the iron-free and iron-containing ettringite phases [14]. Similarly, research by Dunstan [16] and Kalousek et al. [17] have shown that the Fe_2O_3 in class F fly ashes has a moderating effect on the formation of aluminate-rich (iron-free) ettringite mainly responsible for expansion due to sulfate attack.

Although high Fe_2O_3/low Al_2O_3 cement show a significant resistance to sulfate attack, the phenomenon will occur, but only after several years [14,17]. It is also emphasized that these cement do not show significant resistance to $MgSO_4$ attack, only the attack of alkali sulfates [14]. The former was not investigated in the current study. Blaine and

Arni [10] stated that there might be a minor positive correlation between SrO, Cr, Ni, P, and Zn and sulfate attack. However, their study did not have the computing resources to run multivariate analysis. Following up on that work, trace elements were analyzed with other variables in the study presented herein. The trace elements did not show a substantial correlation in this study. While this does not mean that they do no play a role in concrete deterioration from sulfate attack, their role is minor in comparison to other compounds. There is a substantial difference between the study conducted by Blaine and Arni and the research reported herein. Blaine and Arni added gypsum into the mortar samples to provide a sulfate environment to bring about the expansions. This protocol differs from the protocol used in this study, in which samples were soaked in a saturated sodium sulfate solution. Therefore, expansion values are not directly comparable.

7. Conclusions

Improving the durability of concrete is of utmost importance to governmental bodies, contractors, and owners worldwide. Large economic savings can be realized with structures made of more durable, longer-lasting concrete. The results reported herein identify key cement characteristics, which contribute to the resistance of concrete to sulfate environments. Although C_3A content has typically been assumed as the characteristic responsible for the lack of sulfate resistance, this study has confirmed that it is not the primary factor controlling expansion in alkali sulfate environments. The very high negative correlations between both Fe_2O_3 and C_4AF and sulfate attack expansion reveal that the cement with high iron contents are the most beneficial in controlling sulfate attack. The iron-rich ettringite formed from these high-iron cement are not as expansive. The roles of alkalies and alumina are clearly part of the sulfate attack mechanism, but iron has a strong mitigating effect.

Changing specification to require more C_4AF (greater than 7%) to provide sulfate resistance would increase reliability of cement specifications to provide sulfate resistance. While considering alkalies in a model for specifications will improve the prediction, it adds complexity to the specification, especially considering the interaction of alkali with the other properties of cement and concrete.

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