Influence of Portland Cement Characteristics on Alkali Silica Reactivity

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ABSTRACT

The findings of this study which evaluated 21 portland cements identified K_2O and Na_2O_{eq} as significantly contributing to ASR expansion with a less strong correlation to SO_3 content The conclusions are based on results of ASTM C 441 Tests. Response surface modeling has identified a negative trend of clinker SiO_2 and a direct trend of Na_2O_{eq} as significantly contributing to ASR expansion. The ASTM C 227 analytical results were less conclusive and proved to be a poor indicator of the effects of cement variables in the expansion in tests up to 1 year in duration. In contrast, ASTM C 441 rapidly and clearly delineated the cements contribution to ASR expansion.

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INTRODUCTION

Cement manufacture has changed significantly in the past two decades, mainly because of environmental and energy concerns *(1)*. Environmental concerns have resulted in the use of fuels with reduced sulfur; in addition, kiln dust, which is rich in alkalis, is routinely collected and returned to the kiln, resulting in cements with a higher alkali content *(2)*. It is being reported worldwide that modern cements are not as durable as older cements *(3)*. It is reported that excessive expansion of modern concrete subjected to wetting and drying cycles is related to incomplete kiln reactions and that deleterious reactions occur in the larger cement particles *(4)*.

The objective of this investigation was to statistically examine the effects of cement characteristics on alkali silica reactivity of modern concretes. To this end, concretes were prepared as nearly as possible to being identical and allowing only the cement composition to change from one concrete mixture to the other.

ALKALI SILICA REACTIVITY

Alkali silica reaction (ASR) occurs when soluble alkali ions present from the cement, admixtures, or other sources, such as sodium and potassium, react with certain types of silica structures present in the aggregate *(5)*. Examples of silica that make an aggregate potentially susceptible to ASR are strained and microcrystalline quartz, opaline chert, tridymite, cristobalite, and glass. This reaction results in the formation of a silica gel that is capable of imbibing large quantities of water. The gel causes internal stresses, which ultimately result in cracks. The cracks then fill with additional gel, increasing the stress on the microstructure, which forms a "weak link" in the matrix. ASR can be identified on the surface of concrete as a network of cracking called "map cracking." The gel sometimes leaks out of the cracking network onto the surface of the concrete, and appears as a white efflorescence. A slice taken from an affected piece of concrete will reveal that the cracking network can travel through aggregates, and is not limited to the interfacial zone of the matrix *(6)*.

Three conditions are necessary for ASR to occur: (1) a cementitious mixture sufficiently high in soluble alkalis, (2) the presence of a soluble form of silica, and (3) the presence of water. It has also been found that a relative humidity of 80 percent or greater referenced to 21°C to 24°C is required to support the ASR chemical reactions *(7)*. In addition, the chloride ion may contribute to the alkali-silica reaction if it is present in the pore solution in significant amounts *(8,9)*.

The sodium and potassium in cement are present as sulfate phases or contained within the aluminate and silicate phases of the anhydrous cement *(6)*. Some of the potassium sulfate tends to react with the gypsum in cement to form syngenite, $K_2SO_4 \bullet CaSO_4 \bullet H_2O$ *(10)*. Other sulfate forms present in clinkers found in North America are arcanite (K_2SO_4), aphthitalite ($3K_2SO_4 \bullet Na_2SO_4$), and calcium langbeinite ($2CaSO_4 \bullet K_2SO_4$) *(11)*. More than half of the alkalis not in sulfate form are found in the C_3A, C_3S and ferrite in the cement *(10,12)*. It has been found that the effect of ASR (the formation of an expansive gel that contributes to the development of cracking) does not significantly differ with varying source form of alkali.

Higher concentrations of alkalis (K or Na) in the pore water solution encourage greater swelling capacities in the gel. The concentration of sodium and potassium compounds and hydroxyl ions is dependent on the quantity of sodium and potassium compounds in the anhydrous portland cement. The

hydroxyl ion concentration in a saturated solution of calcium hydroxide is 0.04 M or pH = 12.6. The pH of the pore solution in concrete made with low alkali cement ranges from 12.7 to 13.1 and in the case of high alkali cement from 13.5 to 13.9. This means that the hydroxyl ion concentration in the pore solution of concrete made with high alkali cement may be ten times as high as that made with a low alkali cement.

While it is only in pore solutions of high hydroxyl ion concentration that significant attack on reactive silica occurs, Buck et al. found that the reaction of the potassium ion in ASR is more severe than the reaction of the sodium ion *(13)*. The mere limitation of alkali content is not sufficient to limit ASR expansion. In fact, additional alkalis from admixtures and high-alkali pozzolans may have little effect or a beneficial effect on the alkali-silica reaction.

The expansion starts with a reaction of the silicon in the silanol group (Si-OH) with alkali and hydroxyl ions in the pore water and extends to the siloxane group (Si-O-Si) *(14)*. As the Si- bonds are attacked, an isotropic coagulate forms that can imbibe water through osmosis to form an expanding gel *(15, 16)*. Using osmotic theory, the cement paste acts as an impermeable membrane toward the silicate ions. According to*(15)*, the membrane will allow water, hydroxyl ions, and the alkali metal ions to diffuse through it but not the silicate ions. Under these conditions, any reacting site would exert an increasing pressure against the restraining paste.

Studies have shown that free $Ca(OH)_2$ is a requirement for ASR to occur, although the reactive silica may continue to dissolve without free $Ca(OH)_2$. There appears to be a correlation between the C/S ratio of C-S-H in portland-cement pastes and potential deterioration from ASR. Binding C-S-H compounds with lower C/S ratios (or cements with lower C_3S/C_2S ratios) are not as susceptible to deterioration as higher C/S ratio C-S-H compounds *(17)* and higher silica content binders may increase the resistance to ASR deterioration. Therefore, cements with lower C_3S/C_2S ratios produce C-S-H compounds with lower C/S ratios, which are not as susceptible to generating and sustaining ASR attack *(18)*.

The pH of the pore solution is raised by the dissolution of these alkalies, which facilitates a more rapid dissolution of certain silica forms. These soluble silica forms contribute to the expansive silicate gel. The composition of the alkali silicate gel is high in CaO and alkalis, with the CaO content increasing along a crack as one moves away from its source *(6)*.

MATERIALS AND PROCEDURES

The materials used in this study include portland cement, fine aggregate, and crushed Pyrex cullet. The Pyrex cullet used for the ASTM C 441 test was obtained from the original inventory used by the U.S. Bureau of Mines. The fine reactive and non-reactive aggregates were prepared from two materials derived within Pennsylvania. The reactive aggregate is a metamorphosed argillaceous sandstone containing pyrite framboids that was the single most reactive aggregate in the Commonwealth of Pennsylvania as evaluated with AASHTO T-303 test protocol. In addition, its field performance was exceptionally poor. The non-reactive aggregate is a locally derived siliceous sand that tested non-reactive and possesses an excellent field performance history.

Cements

In order to evaluate successfully the effect of cement characteristics on concrete durability, a representative sample of cements with varying chemical components had to be obtained. A survey and sampling of North American cements was conducted with the assistance of the Portland Cement Association. A statistical analysis model based on the design of a weighted central response surface was developed using these data. For this study, twenty-one cements were selected from the 114 type I and II cements manufactured in the United States. Selection was made on a statistical basis to provide a systematic coverage of the range in variability that bounded the extremes of manufactured cements for the following parameters:

Fineness
C_3A
Na_2Oeq
SO_3

Extreme low, high, and mean values of four characteristics were chosen from this analysis: SO_3 content, C_3A content, alkali content, and fineness. Data from the North American survey of cement manufacturer's data revealed typical high, low, average, and extreme values. These values are displayed in Table 1.

Table 1. Analysis of Major oxides and Discriminating Properties for Test Clinker

Cement #	Code #	SO$_3$	alkalis	C$_3$A	Blaine	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	SO$_3$	LOI-950	Na$_2$O	K$_2$O
1	2414	2.830	0.39	5.5	4084	20.91	3.97	2.99	62.97	3.27	2.83	1.46	0.095	0.450
2	2312	2.380	0.52	3.8	3622	21.45	4.01	4.02	64.65	1.39	2.38	0.59	0.199	0.490
3	2403	4.130	0.46	6.4	4048	20.26	4.45	3.20	63.81	1.55	4.13	1.52	0.156	0.460
4	1056	3.770	0.76	11.7	3282	19.79	5.46	1.61	64.49	1.16	3.77	1.64	0.150	0.920
5	1043	2.730	0.46	10.0	3871	20.56	5.02	1.94	63.77	3.77	2.73	1.23	0.090	0.560
6	1016	3.000	0.26	10.0	3831	20.45	5.61	2.90	63.94	1.88	3.00	1.02	0.179	0.117
7	1013	3.040	0.50	11.7	3705	19.81	6.03	2.54	64.46	0.88	3.04	1.37	0.240	0.390
8	1024	3.130	0.64	9.6	4009	20.08	5.47	2.90	63.77	1.15	3.13	2.11	0.121	0.790
9	1039	3.840	0.84	9.3	3871	20.49	5.14	2.54	63.10	1.74	3.84	1.41	0.180	1.000
10	1015	2.810	0.91	7.5	4345	21.12	4.42	2.48	63.89	1.99	2.81	1.44	0.470	0.670
11	1028	4.350	0.92	9.5	4029	19.61	5.25	2.60	62.43	2.11	4.35	1.71	0.200	1.090
12	1051	3.480	0.79	6.7	3950	20.54	4.56	3.18	61.01	5.01	3.48	1.12	0.250	0.820
13	1104	2.680	0.37	5.8	3768	21.33	4.04	2.88	63.85	1.25	2.68	1.52	0.133	0.360
14	1060	2.680	0.50	7.2	3600	21.08	4.70	3.12	63.96	1.22	2.68	1.46	0.096	0.610
15	1027	3.260	0.81	7.8	4179	20.20	4.58	2.59	62.65	2.09	3.26	1.74	0.200	0.930
16	1059	3.050	0.07	9.5	3850	20.77	4.55	1.52	63.71	2.48	3.05	1.46	0.056	0.017
17	1017	3.190	0.86	7.2	3384	21.25	4.29	2.44	63.37	2.04	3.19	0.84	0.390	0.710
18	1007	3.430	1.00	10.6	3663	19.72	5.27	1.97	63.14	3.27	3.43	0.73	0.320	1.150
19	1020	2.730	0.66	9.8	3803	20.29	5.54	2.90	64.97	1.04	2.73	0.70	0.112	0.830
20	2322	2.900	0.39	7.4	3930	20.68	4.84	3.23	64.65	1.85	2.90	0.70	0.038	0.540
21	2334	3.180	0.70	7.3	4104	20.40	4.63	2.91	61.76	3.96	3.18	1.36	0.320	0.570

Using these values as guidelines, AASHTO M85 Type I and Type II cements were selected from a coded manufacturer inventory sheet. Five "average" cements were selected in order to form a basis for comparison. Eight cements were selected as "corner points" for the model to represent high and low value combinations for the characteristics of interest. Another eight cements were selected as "star points" representing the extreme high and extreme low values for each of the four characteristics. The target values of chemical characteristics, are listed in Table 2.

	SO3	Equivalent Alkalis	C3A	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: Target Values for Selected Cement Characteristics

Alkali-Silica Reaction

As part of the NCHRP 18-5 testing, two test protocols to monitor the development of ASR were followed in this study, ASTM C 441 and C 227.

The potential of each cement to contribute to deleterious alkali-silica reactivity was evaluated using ASTM C 441, "Standard Test Method for Effectiveness of Mineral Admixtures or Ground Blast-Furnace Slag in Preventing Excessive Expansion of Concrete Due to the Alkali-Silica Reaction (22)." ASTM C 441 was selected due to its use of the Pyrex glass as a highly reactive aggregate, in an accelerated test which is intended to discriminate between cements. Mortar bars were prepared using a specified gradation of Pyrex glass, which optimizes the reaction resulting in rapid screening of the cements.

For the ASTM C 441 test, the bars were suspended above water, with an adequate fabric wicking system providing a sTable humidity level throughout the sealed outer container to promote the maximum amount of expansion (19).

Three mortar bar samples were prepared for each cement, and a set of control bars was prepared with non-reactive natural sand aggregate as well for comparison. The storage containers were placed in a 38°C chamber for the duration of the experiment. Length measurements were made at the end of a two-week undisturbed time period in the storage container, and subsequently at 4,6,8 and 12 weeks.

ASTM C 227, "Standard Test Method for Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar Bar Method)"(20), was also conducted. This test method requires a much longer duration of time until appreciable results are obtained. For this testing protocol, ten mortar bars were made for each cement: five using the non-reactive standard sand used for other mortar tests, and five using another AASHTO-approved sand deemed to be an aggregate susceptible to the alkali-silica reaction. These bars were sealed in plastic bags with 10 mL of water to provide a 100 percent relative humidity environment and stored in a 38ºC chamber. Length measurements were taken monthly.

Statistical Analysis Procedures

For each independent and dependent variable, several types of statistical analysis were performed using the statistical software program MiniTab. 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 values and p-values were recorded. The data were also evaluated by a centered weighted response surface model in this same software package. The selection criteria for the cements used in this study were based upon this modeling approach.

Limitations on Interpretation

Regression and correlation analysis performed by MiniTab was based upon the "least-squares method" of curve fitting. It can be assumed that for regression equations, the probabilistic model assumes that "the expected value of Y is a linear function of X, but that for fixed X, the variable Y differs from its expected value by a random amount" (21). Therefore, for regression analysis as well as any other curve fitting techniques, there is some form of random deviation or error incorporated into any usage of the equation. The least-squares method attempts to minimize this deviation by fitting a line with minimal vertical distances to actual data points.

The coefficient of determination, or r^2 value, gives a measure of the quality of the fit of the regression equation. Values of r^2 range from 0 to 1, with values approaching 1 providing the best fit to the data. The correlation coefficient corresponds to the value of r, the square root of r^2. The sign of the correlation coefficient is useful in that it reveals whether the best fit line has a positive or negative slope.

RESULTS
Regression Analysis of Alkali-Silica Reaction Data

ASTM C 441 testing was performed in order to evaluate the alkali-silica reactivity of each of the 21 cements (22). An initial length measurement was taken 24 hours after the bars were cast, and subsequent length measurements were taken at 2, 4, 6, 8 and 12 weeks. The general trends of ASR expansion for all 21 cements are determined from this data, Table 3.

The results from regression analysis performed on week 2 measurements have shown that total equivalent alkali content and K_2O content are the prime correlated factors, Figure 1 contrasts the statistical behavior of K_2O and Na_2O with ASR expansion. Figure 1 shows a strong correlation between expansion and total equivalent alkali and weaker correlation with SO_3. The week 4 expansions exhibit similar behavior to that noted in the 2 week data sets, as shown in Table 3. It was shown that total equivalent alkali content and K_2O content continue to be the dominant factors controlling expansion. Na_2O content [singly] begins to show a stronger relationship, while the r^2 value for SO_3 becomes lower

At 8 weeks, total equivalent alkali content and K_2O appear to be the only two significant contributors to alkali-silica expansion. The regression results reveal that all other cement characteristics have significantly lower r^2 values. The majority of the 21 cements showed no additional expansion between the 8-12 weeks of exposure periods, consistent with the use of the 14-day period as a test criterion for estimating expansion.

Single variant analysis of these cements suggests that the single most important chemical factor related to the maximum expansion is equivalent Na_2O. The cements that show the maximum expansion have high equivalent Na_2O (above 0.70). Exceptions to this are the cements 17 and 21. These cements have equivalent Na_2O above 0.70 % but their expansions are not large and lack of expansion could not be correlated to any other property except SiO_2. Both have relatively high SiO_2 contents [low C_3S/C_2S ratios] which may reduce the otherwise anticipated expansion.

According to this preliminary observation, the second most important chemical factor linearly correlating to the ASR expansion was found to be the SO_3 content of portland cement, although the r^2 value was low. All the cements that show high expansion have SO_3 content above 3.25 %. The only exception to this was the cement # 3. This cement has very high SO_3 (4.10 %), but low alkali. SiO2 data showed a slight negative correlation. There was no correlation observed between C_3A, Blaine and ASR expansions. The cements that show high ASR have reasonably high Blaine fineness (exception # 4), but high Blaine fineness by itself does not have any relation to on ASR, if equivalent Na_2O was very low. Cement # 8 can be cited as an example to prove the above observation. These observations suggest that there may be a combination of factors responsible for ASR in concrete.

Table 3. ASR Mortar Bar Expansion at Various Exposures by ASTM C 441 Test

Sample Code						ASR Expansion (%)				
Cement #	PCA #	SO_3	Eq. Na_2O	C_3A	Blaine Fine-ness	2 week	4 week	6 week	8 week	12 week
1	2414	2.83	0.39	5.50	4084	0.01	0.01	0.01	0.01	0.01
2	2312	2.38	0.52	3.80	3622	0.10	0.12	0.12	0.13	0.12
3	2403	4.13	0.46	6.40	4048	0.16	0.19	0.18	0.19	0.18
4	1056	3.77	0.76	11.70	3282	0.36	0.39	0.39	0.39	0.24
5	1043	2.73	0.46	10.00	3871	0.05	0.07	0.07	0.07	0.07
6	1016	3.00	0.26	10.00	3831	0.00	0.00	0.01	0.02	0.01
7	1013	3.04	0.50	11.70	3705	0.18	0.22	0.22	0.22	0.22
8	1024	3.13	0.64	9.60	4009	0.20	0.21	0.28	0.22	0.22
9	1039	3.84	0.84	9.30	3871	0.32	0.34	0.36	0.36	0.37
10	1015	2.81	0.91	7.50	4345	0.30	0.39	0.40	0.41	0.50
11	1028	4.35	0.92	9.50	4029	0.36	0.37	0.37	0.38	0.43
12	1051	3.48	0.79	6.70	3950	0.24	0.28	0.27	0.22	0.28
13	1104	2.68	0.37	5.80	3768	0.00	0.01	0.01	0.02	0.01
14	1060	2.68	0.50	7.20	3600	0.08	0.09	0.09	0.09	0.09
15	1027	3.26	0.81	7.80	4179	0.37	0.38	0.37	0.38	0.38
16	1059	3.05	0.07	9.50	3850	0.01	0.01	0.00	0.01	0.00
17	1017	3.19	0.86	7.20	3384	0.22	0.24	0.24	0.24	0.24
18	1007	3.43	1.00	10.60	3663	0.35	0.37	0.38	0.38	0.38
19	1020	2.73	0.66	9.80	3803	0.13	0.14	0.14	0.14	0.14
20	2322	2.90	0.39	7.40	3930	0.02	0.02	0.02	0.03	0.02
21	2334	3.18	0.70	7.30	4104	0.15	0.18	0.19	0.19	0.19

Combination of Minor Oxides and Trace Elements

  Combined minor and trace elements show a very strong correlation to 2, 4, and 6-week expansions when combining 8 or 9 factors. However, if we see the r^2 value for the individual elements or for any combination of these elements except chlorine, it is very clear that there was no significant correlation between the individual trace elements and the ASR expansions (*22).*

Combination of Physical and Chemical Characteristics of the Cement

  A strong single variable correlation between equivalent Na_2O and ASR expansion is shown at all ages. Equivalent Na_2O and SO_3 combinations show a very strong correlation to 2, 4, and 6 weeks ASR expansions. ASR expansion data at 2 weeks is plotted against the SO_3 and equivalent Na_2O content of cements in Figure 1. Equivalent Na_2O shows a positive correlation to 2 week ASR expansion with r^2 values of 0.798. The correlation between the 2 week ASR as a function of SO_3 and equivalent Na_2O content of cements plotted in Figure 2. According to this plot, K_2O shows a higher single-variable correlation to ASR than Na_2O. However, the highest correlation obtained is still for total equivalent Na_2O rather than the individual alkalis. This suggests that controlling the total alkali content is more important for controlling ASR. Low r^2 values for the combinations in which equivalent Na_2O and SO_3 are not one of the variables show that, C_3A, Blaine fineness and C_3S/C_2S ratio have relatively little influence on ASR expansion.

Combination of Major Cement Phases

  There is minimal correlation between the major portland cement phases and ASR expansion for Multi-regression and single-regression analysis data for the dependency of ASR expansion on the combination of $C_3S + C_2S + C_3A + C_4AF$[22].

Response surface modeling

  When these data were subjected to the full multi-variant non-linear modeling, only the equivalent alkali and the silica content of the clinker exhibit any significant correlation. Figure 3 is the three-dimensional model surface of this response with the individual data points noted which generally details the trend of increased expansion with increasing equivalent alkali and decreasing silica content of the clinker. A response surface model, Figure 4, was fit to these data, which yielded the following relationship:

$$\% \text{ Expansion} = 1.05934 + 0.47883\ Na_2O_{eq} - 0.05634\ SiO_2$$

ASTM C 227 results

  The ASTM C 227 specimens were evaluated after 6 and 12 months of processing. The data that were collected, analyzed and found not to provide any differentiation among the twenty-one cements even though the aggregate used in the study represented the single most reactive aggregate in the Commonwealth of Pennsylvania with a poor performance history in field use *[22]*.

DISCUSSION

  The results of the analysis of single variable parameters confirm the long held observation *[15*] that the alkalis are principal contributors to ASR deterioration. Potassium is notably more important than sodium but both contribute to form a significant effect. The strongest correlation is still with total molar equivalent alkali. The statistical treatment of these results has also flagged sulfatebut with a much poorer correlation, which can be primarily identified as tracking the alkali content, the coupled major source of the sulfate in the cements.

  The role of cement-silica on ASR expansion has received very little consideration in the literature [17]. What few studies that have been conducted suggest that the C_3S/C_2S ratio of the cement potentially controls the C/S ratio in the C-S-H, which in turn has a variable susceptibility to ASR attack by indirectly controlling the formation of CH, a minimum amount of which is necessary for ASR attack. The multi-
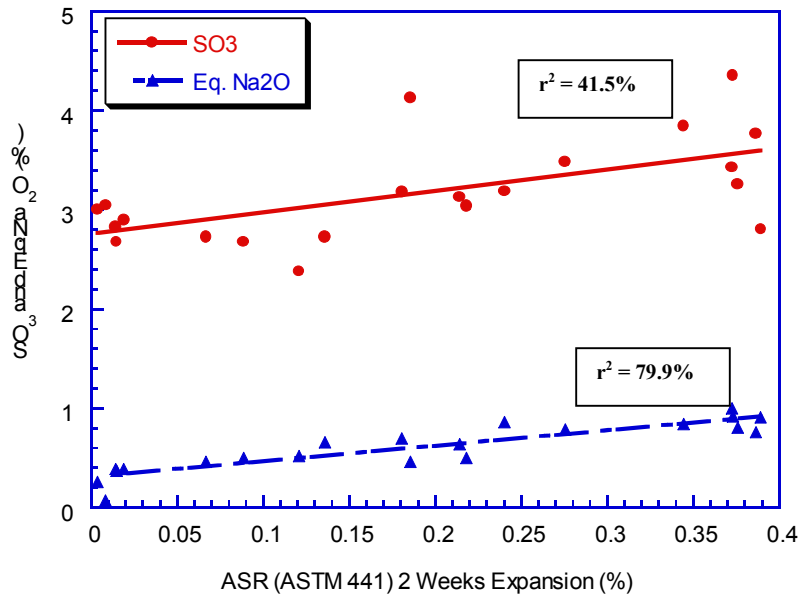
Figure 1. ASR Expansion at 2 Weeks (ASTM C 441 Test) versus Na_2O_{eq} and SO_3 Content of Portland Cements.
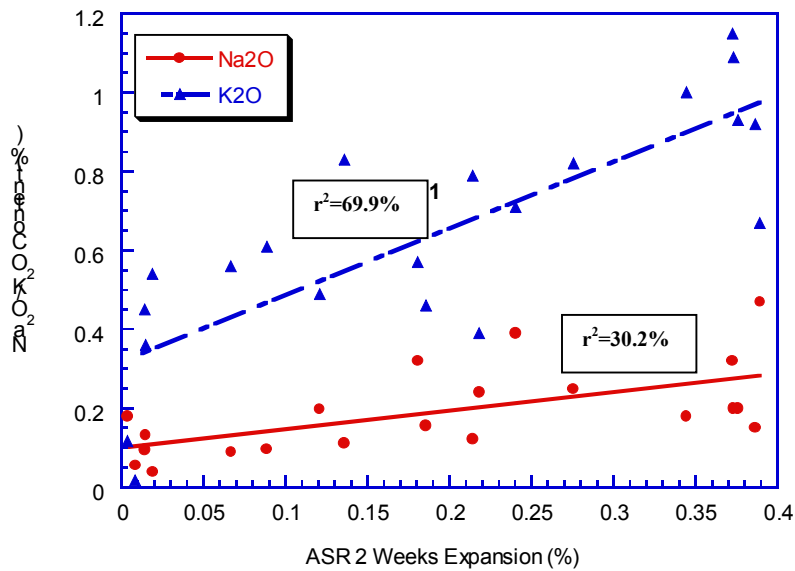

Figure 2 ASR Expansion at 2 Weeks (ASTM C 441 Test) versus Na_2O and K_2O Content of Portland Cements
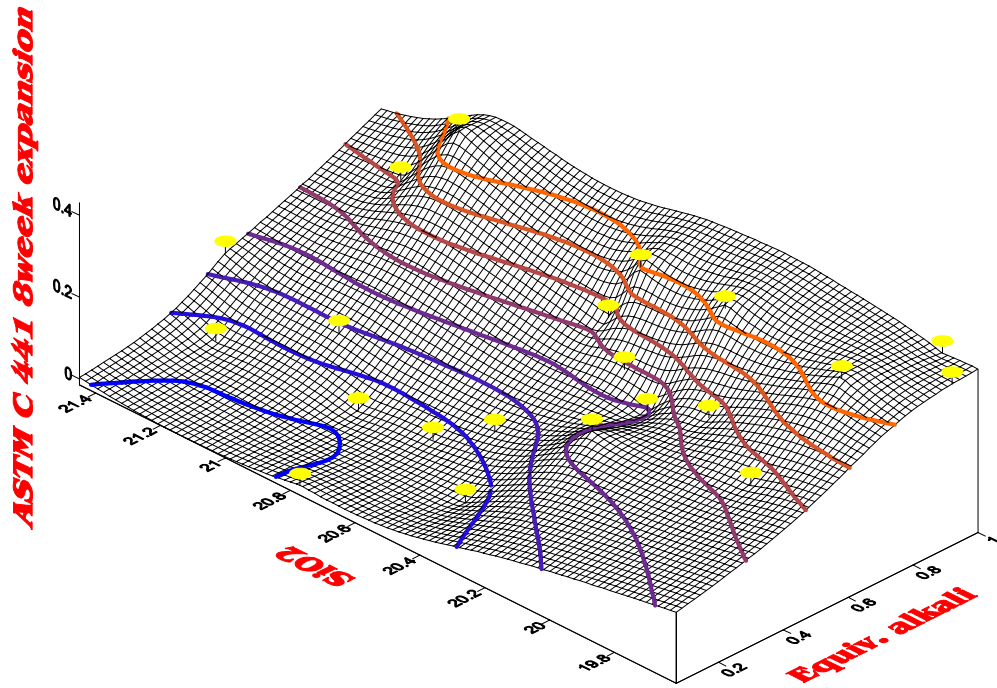
Figure 3. Surface modeling of C 441 expansion as a function of SiO₂ and Na₂O_{eq}.
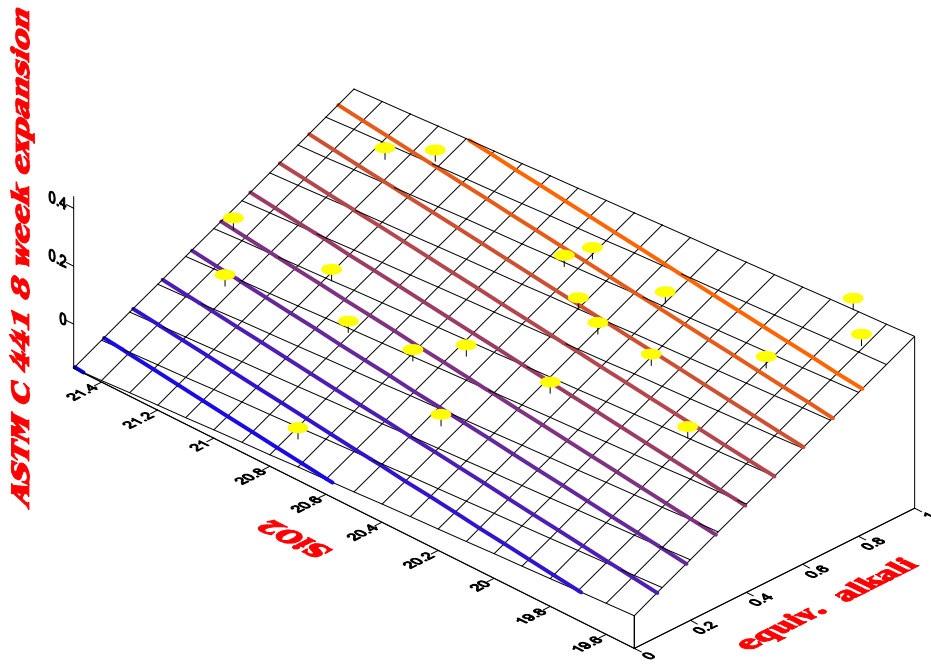
Figure 4. Response surface modeling of C 441 expansion as a function of SiO₂ and Na₂O_{eq}.

The implications derived form these observations, designed to explicitly examine primarily the effect of the cement chemistry, goes directly to the compositional control over the manufacture of cements.variant response surface modeling supports these observations with a significant correlation between equivalent alkali and a negative correlation to silica. Interestingly, the correlation is indirectly related to the C_3S/C_2S ratio, which when tested as a single variable, tested at a relatively low significance level. When combined with the Na_2O_{eq}, it was very high.

Additionally, this study found that the C 227 testing protocol does not effectively discriminate cements on reactivity, at least within the one-year term of our testing. C 441 appeared to be more much more discriminating as a test for evaluating cements, having the further advantage of only requiring short term testing.

CONCLUSIONS   The results of this study on a statistical survey and study of Type I and Type II cements that are manufactured throughout the United States using ASTM C 441 tests showed that these findings are supported by previous observations on isolated examples of cement, that indeed the potassium oxide content of the cement is important in determining the expansion with expansive aggregates. The study further determined that total equivalent alkali, Na_2O_{eq}, however, more strongly correlates to expansion confirming the contribution from sodium to the overall expansion. When viewed in context with all of the 75 variables examined in this study, the silica content of the cement in combination with Na_2O_{eq} demonstrated the most contribution to expansion. Cements with lower C_3S/C_2S ratios produce C-S-H compounds with lower C/S, which do not contribute as greatly to ASR as has been noted by *(18)*.
This study observed that the ASTM C 227 test when used with a highly reactive natural aggregate did not discriminate between the different cements in tests up to 1 year. A better discriminating test protocol is ASTM C 441.

ACKNOWLEDGEMENTS

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