STATE OF CALIFORNIA

DEPARTMENT OF TRANSPORTATION

DIVISION OF ENGINEERING SERVICES

MATERIALS ENGINEERING AND TESTING SERVICES

OFFICE OF RIGID PAVEMENT MATERIALS AND STRUCTURAL CONCRETE

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<u>INTERIM REPORT</u>

USE OF RAW LIMESTONE IN PORTLAND CEMENT

January, 2008

USE OF RAW LIMESTONE IN PORTLAND CEMENT

This report reflects the observations, findings, conclusions, and recommendations of the authors.

This report does not constitute a standard, specification, or regulation. The Office of Rigid Pavement Materials and Structural Concrete is responsible for the accuracy of the information and data presented in this report.

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Summary

In May 2004, ASTM adopted revisions to the C 150 Standard that allows for up to 5 percent raw limestone as an ingredient in portland cement. Caltrans has performed a literature study and determined that no sufficiently large-scale test program has been carried out to indicate whether cements with and without raw limestone are in fact statistically equivalent to one another with respect to performance and durability. This conclusion is especially true with respect to the medium- to long-term performance of concretes using typical California Type II/V portland cements with 25 percent Class F fly ash—the standard California mix design for pavements and structures.

In August of 2007, Caltrans launched a statistically designed study to evaluate the effect of raw limestone incorporated into portland cement on concrete performance indicators. This study is being performed with the cooperation of the both the California-Nevada Cement Association (CNCA) and the Portland Cement Association (PCA). In accordance with the desires of CNCA members and the PCA, only raw limestones that have been interground with cement are included in the study, rather than separately ground and blended in the laboratory. The study is designed to cover the three primary pillars of medium- to long-term concrete performance and durability: *strength, drying shrinkage,* and *permeability*. Other factors are also examined, including modulus of elasticity, workability (water demand), and actual (baseline corrected) versus ASTM C 150 determined limestone content.

At this time, only data up to 91 days in age are available. The interim results of this study indicate that with the addition of limestone: a) the short-term compressive strengths (through 91 days) are mildly improved; b) permeability, as measured by electrical conductivity, is improved; and c) drying shrinkage is affected negatively.

It is anticipated that the potentially detrimental effect of increased drying shrinkage can be mitigated by appropriate performance-based specifications or changes to design practices. For example, a performance-based specification might specify a maximum or range of drying shrinkage that is permitted in trial batched concrete mixtures. Examples of modified design practices include reducing slab lengths on pavements and adjusting for increased moments in columns of cast-in-place structures.

Design Matrix

Table 1 shows the target design test matrix. Each cell in the matrix represents a sufficient number of repeated laboratory tests to ascertain statistically significant (p-value ≤ 0.05) test parameter differences of 2½ percent or more, in either direction, with a probability of 95% or better. Out of a dozen or so existing California cement plants, it was anticipated that six or more would be able to participate in this study, with at least three of these intergrinding around 4½ percent limestone and the other three producing cements containing roughly 3½, 2½, and 1½ percent interground limestone levels.

In order to ascertain whether the desired properties are a function of the level of raw limestone in the cement, the three plants producing the cements with about 4½ percent interground raw limestone were to be diluted with limestone-free portland cement from the same plant. This aimed to achieve the desired range of limestone percentages shown for cements A, B, and C in Table 1, while the remaining three plants were to be tested only at their optimal[1] percentage and without any interground raw limestone. The control mixture in all cases was the limestone-free portland cement provided by the same plants, using the same clinker.

Accordingly, each plant was asked to produce two cements, one with and one without limestone, from the same clinker. Additionally, three of the participating plants were asked to target the high end of what they considered would be their operating range for limestone content. Naturally, it was not expected that the "target" design matrix would be precisely achieved in terms of the interground limestone percentages shown in Table 1.

Table 1. Target design test matrix

Cement source	Limestone percentage				
	0	1.5	2.5	3.5	4.5
A	×	×	×	×	✖
B	×	×	×	×	✖
C	×	×	×	×	✖
D	×	✖			
E	×		✖		
F	×			✖	

Notes:
×: target limestone percentage
✖: optimum limestone percentage

[1] Optimal limestone content is the amount of limestone that a producer of cement considers to be the proper amount to include in the cement giving consideration to all aspects of cement production and conformance with specification requirements.

Since only five cement sources were finally able to participate in the study, a new design matrix was established using the reported limestone percentages from these five plants shown in Table 2.

Table 2. Actual design matrix

Cement source	Limestone percentage					
	0	1.6	2.2	2.85	3.5	4.2
E	×	×	×	×	×	✖
I	×	×	×	✖		
A	×	×	×	✖		
M	×			✖		
G	×	✖				

Notes:
×: target limestone percentage
✖: optimum limestone percentage

Subsequent testing was carried out "blind" by three participating laboratories: Translab (Caltrans) in Sacramento, Twining Labs of Southern California in Long Beach, and CTL Group, Inc, in Skokie, Illinois. All testing is being conducted in a random and unknown order, and all mix designs were identical for all tested cements. The differing identifying letters representing the cement sources in Table 2 are a result of the blind testing program.

The advantages of the altered design matrix shown in Table 2 are that a greater number of repetitions could be conducted within each cell in the matrix for the same cost and that one additional limestone percentage (five limestone levels instead of the original four) for cements, E, I, and A could be tested. The disadvantages are that only five cements sources could be tested and only one of these five cements has an actual (baseline corrected) limestone content greater than ~3 percent (Cement E). Thus the subsequent data analyses shown in the following sections are not well represented for raw limestone contents greater than 3 percent. It is therefore difficult to draw general conclusions about actual interground limestone levels greater than 3 percent based on this study.[2] It is noteworthy that, as a practical matter, not many plants can add more than 3 percent actual (raw) limestone. The limestone contents determined in accordance with Specification ASTM C 150 will always be higher than the actual raw limestone content because the CO_2 in the base cement is also counted as limestone. See Table 3 for

[2] Throughout this report (except Figure 7), data are presented as a function of actual, raw limestone content in the cement rather than the values determined using ASTM specification procedures which currently include the so-called "phantom limestone" as shown in Figure 7.

the differences in the cements used in this study. Also refer to the discussion below, under the report heading **Secondary Parameters**.

Table 3. Limestone content determinations (average values)

Cement source	Limestone content, percent		
	Apparent limestone in baseline cement (without limestone)	Determined limestone in cement with limestone (per ASTM C 150)	Actual raw limestone content (difference)
A	1.24	3.75	2.52
E	0.91	5.13	4.22
G	2.00	3.43	1.43
I	1.02	3.95	2.93
M	2.93	4.36	1.43
Mean	1.62	4.13	2.51

The Three Pillars of Concrete Durability

Caltrans is especially concerned about medium- to long-term concrete properties that can affect the durability and long-term performance of concrete in the State of California. Drying shrinkage is an equally important concern at any age. Accordingly, since this is a study of the effect of up to 5 percent raw limestone in cement on durability and longevity in our public pavements and structures, all other mix design variables were held constant.

For Caltrans, the three major pillars of concrete durability are:

1) *Strength*—long-term compressive strength, also related to flexural strength and design life.
2) *Shrinkage*—drying shrinkage, related to premature cracking and crack width.
3) *Permeability*—long-term access to moisture and chloride ingress, related to rebar corrosion and premature failure.

In order to ascertain whether the above properties are a function of the level of raw limestone, the three plants (E, I and A) producing the highest interground percentages of limestone were diluted with limestone-free portland cement (from the same clinker). This aimed to achieve the test matrix design percentages shown in Table 2, while the two remaining plants (M and G) were used only at their manufactured raw limestone level and without any limestone, also as shown in Table 2.

Strength

Caltrans traditionally uses flexural strength tests to ascertain the strength of pavement concrete and 6 in. × 12 in. cylinders for strength of structural concrete. In order to make the test program feasible using laboratory sized concrete batches, compressive strength tests were performed using three 4 in. × 8 in. cylinders, each at a variety of test ages from 7 days to 2 years. Modulus of elasticity tests using ASTM C 469 were run only on select cylinders to confirm stiffness properties.

To-date, compressive strength testing has been completed through 91 days, with the 6-, 12- and 24-month tests still remaining.

Shrinkage

Drying shrinkage is being measured by various test methods and mixtures, as follows:

- Concrete unrestrained drying shrinkage using AASHTO T 160 on 3 in. × 3 in. × 11 in. prisms cured at 100 percent relative humidity (RH) for 7 days prior to initiation of drying.
- Concrete restrained drying shrinkage using ASTM C 1581 – the "Ring" Test.
- Mortar drying shrinkage using California Test 527 with 25 percent fly ash.
- Mortar drying shrinkage using California Test 527 without fly ash.

Nearly all drying shrinkage tests apart from ASTM C 1581 (the Ring Test) have been completed to-date. Meanwhile, very few Ring Tests have been completed.

Permeability

Permeability is being measured by the two following test methods:

- Chloride diffusion using ASTM C 1556 at 1- and 2-year test ages.
- Rapid chloride penetration using ASTM C 1202 at 28-day and 1-year test ages.

Specimens for these two tests were cured for 7 days at 23°C & 100 percent RH followed by 21 days @ 38°C & 100 percent RH prior to testing or chloride exposure. The 1-year C 1202 specimens are being stored at 23°C & 100 percent RH.

All 28-day rapid chloride tests have been completed. Meanwhile, the 1-year tests are more than 6 months away, while the ponding samples by necessity all remain untested.

Test Matrix Variables

In an effort to limit the number of test variables, the following mix design properties were held constant:

- Identical mix designs (same mixture ingredients and proportions).
- Constant slump for concretes; constant water/cementitious ratio for mortars.

- Constant fly ash type and percentage (25 percent), except one set of mortars (with no fly ash).

The input variables studied consist of:

- Limestone percentage (a range).
- Cement source (five).
- Testing laboratory (three).

The output variables studied consist of:

- Compressive strength.
- Concrete drying shrinkage (free and restrained).
- Drying shrinkage of mortars (with and without limestone).
- Water/cementitious ratio of concretes (at a constant slump).
- Flow of mortars (at a constant water/cementitious ratio).
- Modulus of elasticity.
- Chloride permeability (both ponding and rapid).

Interim Test Results

<u>Compressive Strength</u>

The compressive strengths through 91 days appear to be better for most of the cements containing raw limestone compared to the control mixtures. Since the long-term tests have not been completed, no conclusions can yet be reached on long-term strengths.

The laboratory effect on the compressive strength test results is depicted in Figure 1. Large data points indicate that the ratio between the cement containing raw limestone and the limestone-free cement are statistically different from unity. In other words, the average strength ratio of cements containing raw limestone is stronger by roughly 5 percent than the limestone-free cements at 7, 28, 56 and 91 days of testing. Furthermore, there is very little difference in these test results between the three testing labs.

In all graphs that follow in this report, any ratio <u>greater</u> than unity indicates that cements containing raw limestone are superior to limestone-free portland cements for the variable indicated in each graph. Conversely, ratios <u>less</u> than unity indicate that cements containing raw limestone are inferior to limestone-free portland cements.

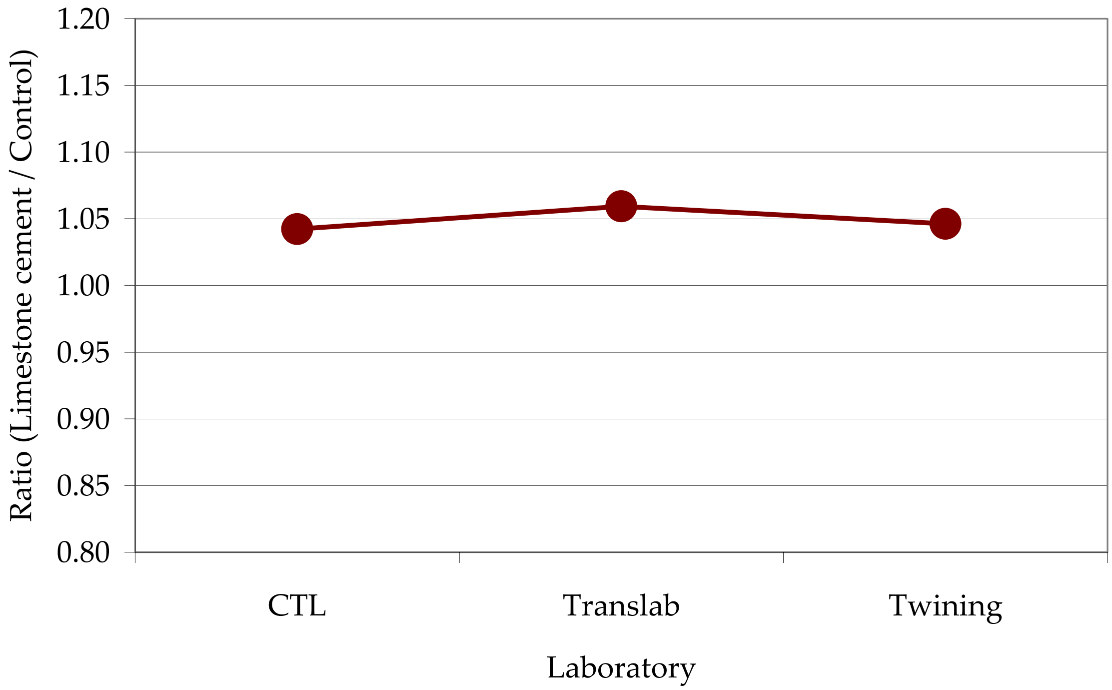

Figure 1. Mean compressive strengths ratios (≤ 91 days) as a function of testing laboratory.

Figure 2 indicates that cements containing raw limestone have higher compressive strengths at all four test ages through 91 days. Cements containing raw limestone are more finely ground than their limestone-free portland cement counterparts, since limestone is much softer than clinker—thus a somewhat finer powder with a broader size range results from the same grinding energy than when limestone is not present. This can assist in early development of strengths due to improved particle size distribution and packing.

Figure 3 shows the average strength ratios for the five cement sources plotted as a function of limestone percentage; all test ages and the data from all three laboratories are combined. As shown, the medium-term compressive strengths actually increase as a function of limestone content. While cement M increases slightly, the difference between the cement M containing raw limestone and the limestone-free portland cement from that source is not statistically significant, as indicated by the smaller size of the data point.

This pillar of concrete durability and longevity indicates that there is no problem with the use of up to 5 percent limestone, for all five cement sources, through 91 days of compressive strength tests. Nothing more can be concluded for later testing ages until the three remaining ages (6, 12, and 24 months) have been tested.

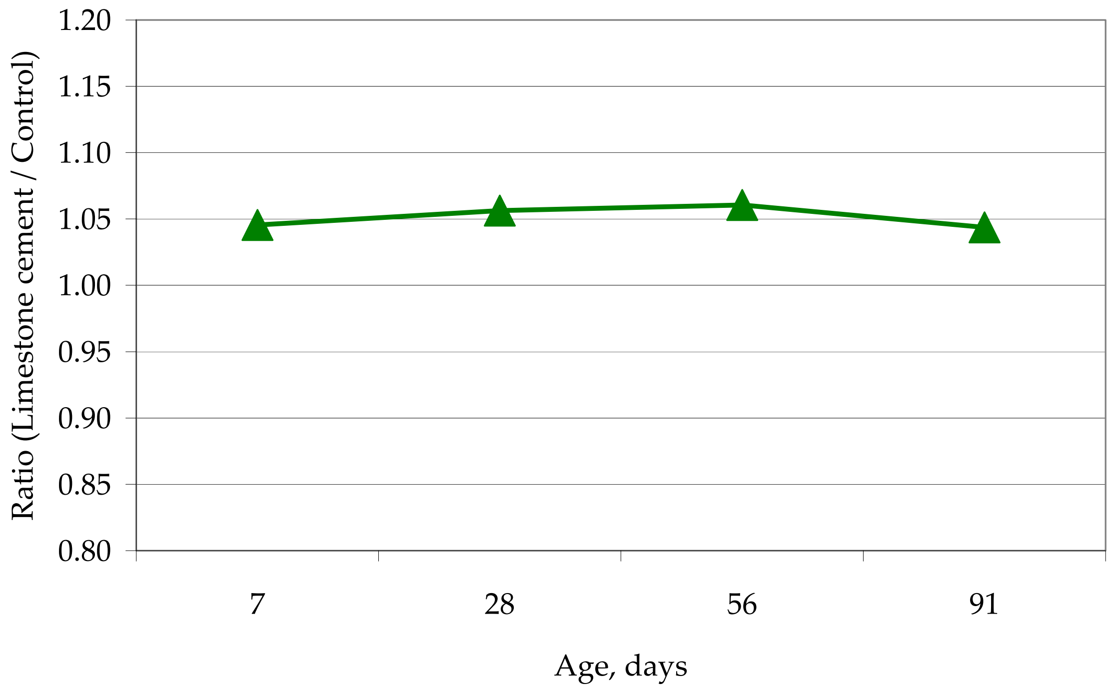

Figure 2. Compressive strengths ratios (≤ 91 days) as a function of age of test.

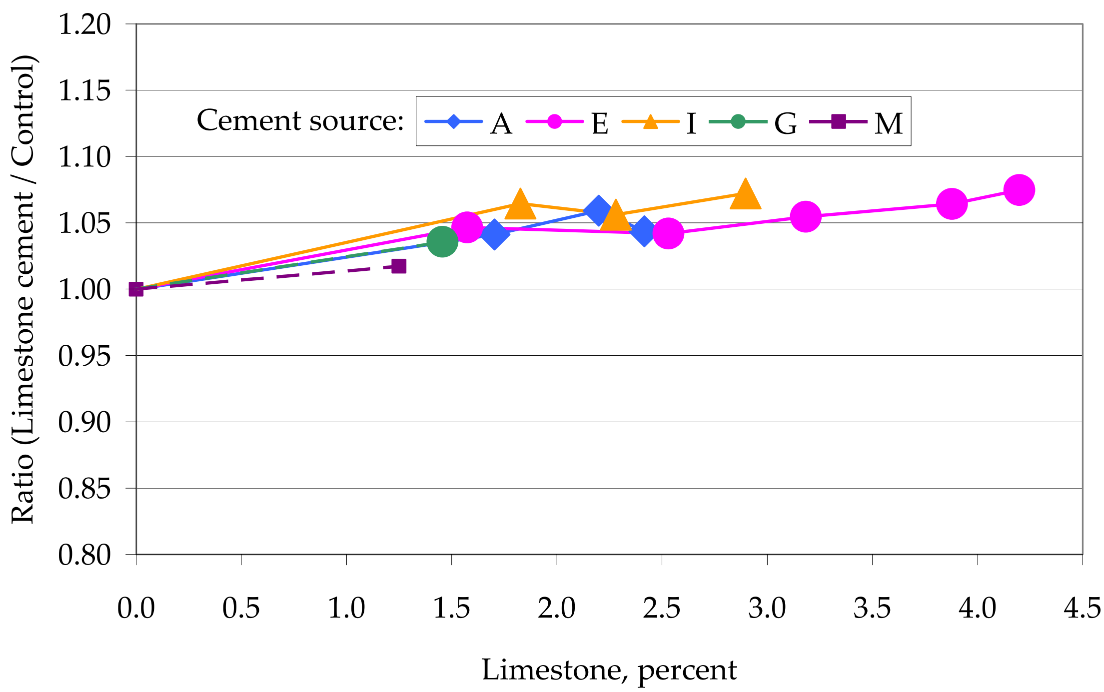

Figure 3. Compressive strengths ratios (≤ 91 days) as a function of cement source and limestone percentage.

Shrinkage

Concrete drying shrinkage ratios after 28 days of drying are significantly better from a statistical viewpoint for most of the limestone-free portland cement control mixtures compared to their limestone-cement counterparts. All concrete drying shrinkage tests using ASTM C 157 prisms have been completed.

The laboratory effect on the concrete drying shrinkage test results is shown in Figure 4. As can be seen, the average shrinkage ratio from two of the three laboratories is nearly the same, while one of the laboratories indicates a small difference. Since only one of the nine "rounds" of repeated testing was performed by the laboratory with this difference, all data was combined for the following analyses with little overall effect on the results.

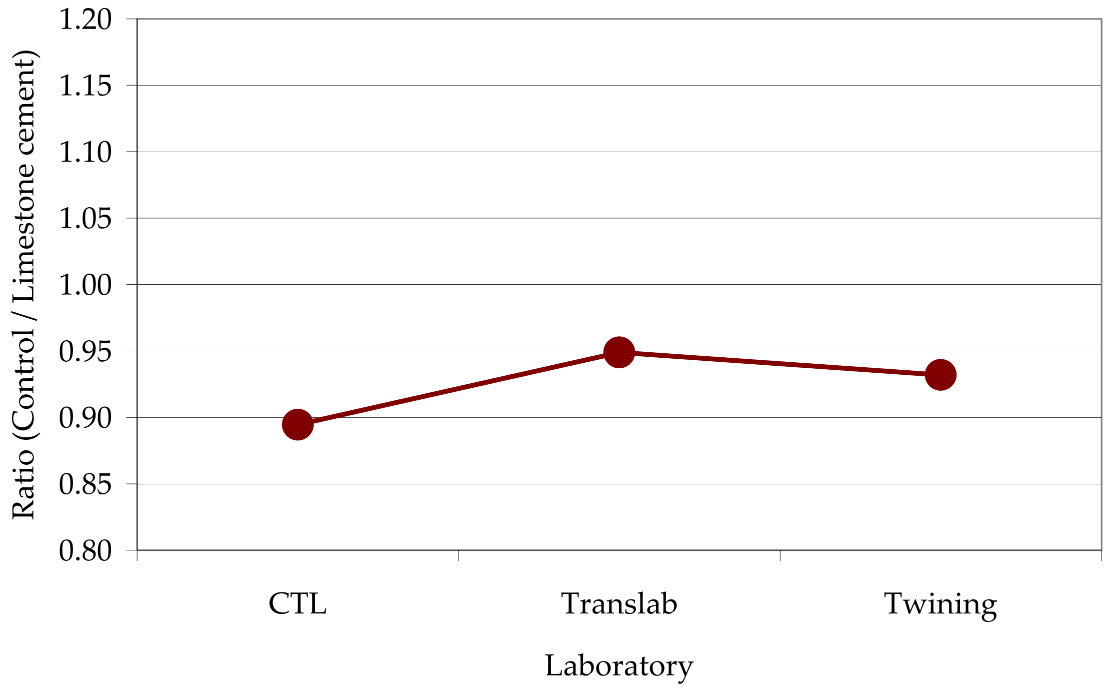

Figure 4. Concrete drying shrinkage ratios (≤ 91 days) as a function of testing laboratory.

Figure 5 shows the average shrinkage ratios for the five cement sources plotted as a function of limestone percentage; all test ages and the data from all three laboratories are combined.

To reiterate, *large data points indicate that the ratios are statistically significant with a p-value of < 0.05. This means that the result is not likely due to random variations in the data.*

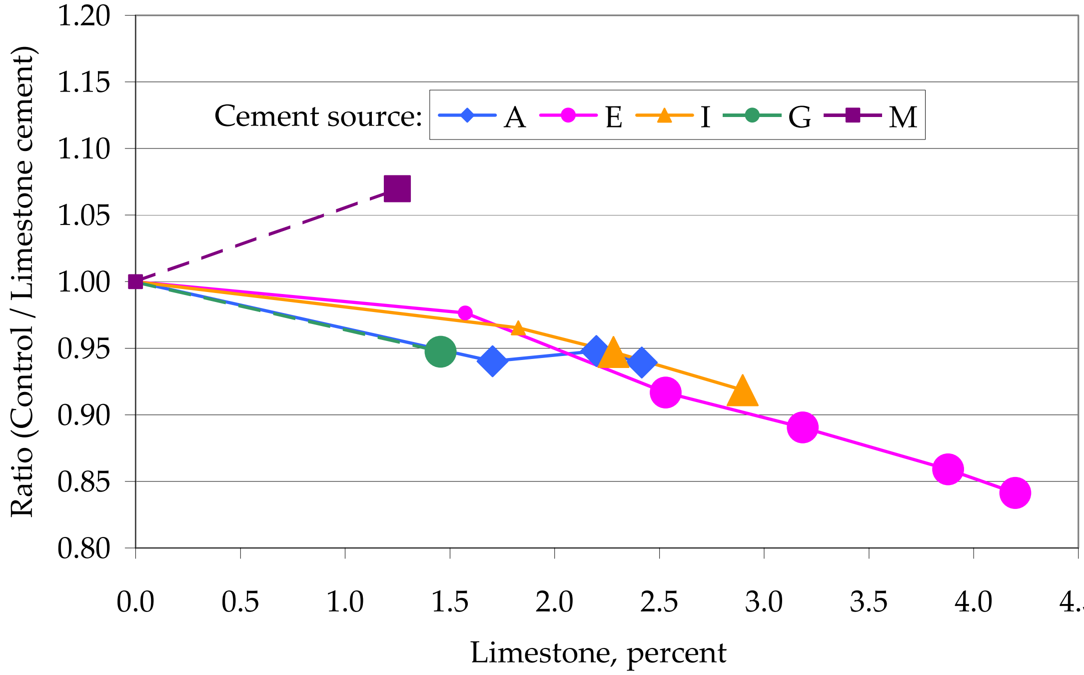

Figure 5. Concrete drying shrinkage ratios as a function of cement source and limestone percentage.

Figure 5 indicates quite clearly that for four of the five cement sources, when cement is made containing raw limestone, these cements performed poorer than when limestone is left out. One exception indicates the opposite—that cement, from source M, performed better in drying shrinkage when raw limestone was interground with the plain portland cement clinker.

It is not known, however, whether these statistically significant differences in concrete drying shrinkage are meaningful in terms of their absolute values of shrinkage. A graph of the actual shrinkage values from the data shown in Figure 5 is presented in *Appendix A*. When reviewing the drying shrinkage levels shown in *Appendix A*, however, it should be kept in mind that only a single mix design was involved in this test program. Other mix designs and/or cements will produce differing results. If drying shrinkage is an issue for a particular application, concrete shrinkage should be measured through trial batches using the actual mix design, cement, and other material sources intended for use in the project.

A newer ASTM test method, called the "Ring" Test (ASTM C 1581), is currently underway. However, insufficient data has been generated to report on the Ring Test results at this time. The Ring Test is a constrained drying shrinkage test conducted in such a manner so that cracking due to shrinkage is induced whenever the mixture's tensile strength is exceeded by the shrinkage of the concrete around a stiff, steel "ring."

Both the rate of stress development and the time to cracking are measured and recorded by this test method.

The test results resulting from drying shrinkage of mortars made with and without limestone additions are also reported in *Appendix A*, as well as the actual shrinkage values of 4-day mortars without fly ash.

Permeability

Planned, long-term permeability tests are by necessity incomplete. Only ASTM C 1202 (Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration) at a testing age of 28 days has been completed, by one of the three testing laboratories involved in this study. Figure 6 shows the results of these tests, which indicate that cements containing raw limestone are less conductive than limestone-free cements. The implication is that the concrete will be more resistant to chloride penetration and damage to the rebar used in concrete. All of the concretes made in this study have permeability ratings according to test method ASTM C 1202 of "low" and "very low"; this is expected from concrete containing 25 percent Class F fly ash. Evidently, based on the data shown in Figure 6, resistance increases with increasing limestone content. It is not known if these changes in resistance are due to decreased permeability or to changes in pore water ion concentration. Diffusion coefficient testing using ASTM C 1556—the "Ponding" Test—will directly measure the ability of chloride ions to penetrate the concrete, which is the issue of concern currently under evaluation. Diffusion coefficient testing will be completed before December 2009, with the earliest test results available in December 2008.

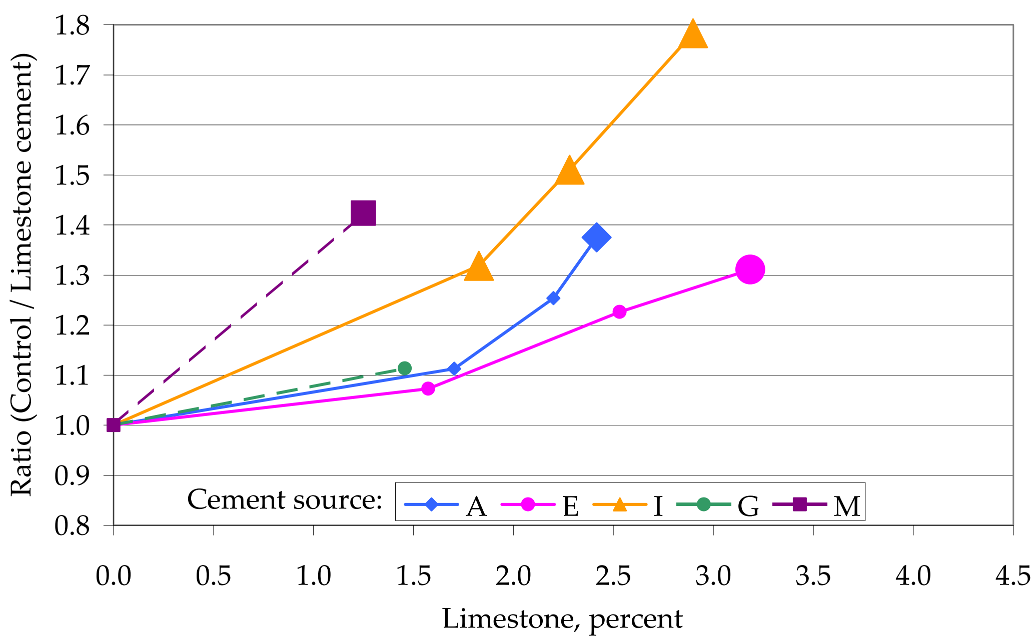

Figure 6. Rapid chloride permeability as a function of cement source and limestone percentage.

Secondary Parameters

Secondary parameters evaluated include modulus of elasticity (MOE), workability (water demand), as well as actual versus ASTM C 150 determined limestone content.

The water demand to achieve a certain slump range for concrete and the flow of mortars when the water/cementitious ratio is fixed indicated no statistically significant differences between limestone-free portland cements and cements containing raw limestone. *Appendix B* provides the necessary detail on this aspect of the blind testing program.

No statistically significant differences were noted from the MOE tests conducted between the limestone-free portland cements and cements containing raw limestone tested. *Appendix C* provides the necessary detail of the limited MOE tests conducted.

As previously stated, the ASTM C 150 values for limestone content are based on the total CO_2 content of the cement, with the assumption that all CO_2 in the cement is due to the presence of limestone. As was confirmed in this study, baseline cements without limestone contain measurable amounts of CO_2. The ASTM standard includes this so-called "baseline CO_2" as part of the apparent limestone in cements with limestone[3].

The differences between the two (baseline corrected limestone and apparent limestone) are significant. Tests—split loss of ignition (SLOI)—were run on cement samples that had been homogenized, blended, sampled, and shipped. Processing, handling, and shipping expose cements to CO_2 in the air, some of which reacts with the cement whether it contains limestone or not. ASTM C 114 tests that determine the CO_2 content of portland cement measures <u>all</u> CO_2 in the cement, which is then used in calculations provided in ASTM C 150 to determine the limestone content as applied in the specification. Figure 7 shows the impact of the baseline CO_2 on the calculated limestone content, as it appears as "phantom limestone" when the CO_2 content is converted to apparent limestone content.

Appendix D contains an additional table showing the differences noted between the actual and targeted limestone contents of the five cements used in this study. As can be seen, the difference between these limestone percentages can be as high as 0.5 percent. Additionally, the limestone content determined using the SLOI test method was at least 0.9 percent greater than the actual limestone content shown in Table 3.

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[3] Sources of baseline CO_2 in portland cements include the CO_2 absorbed from the atmosphere during storage of clinker or transportation of cement as well as from impurities in the gypsum added to control setting time.

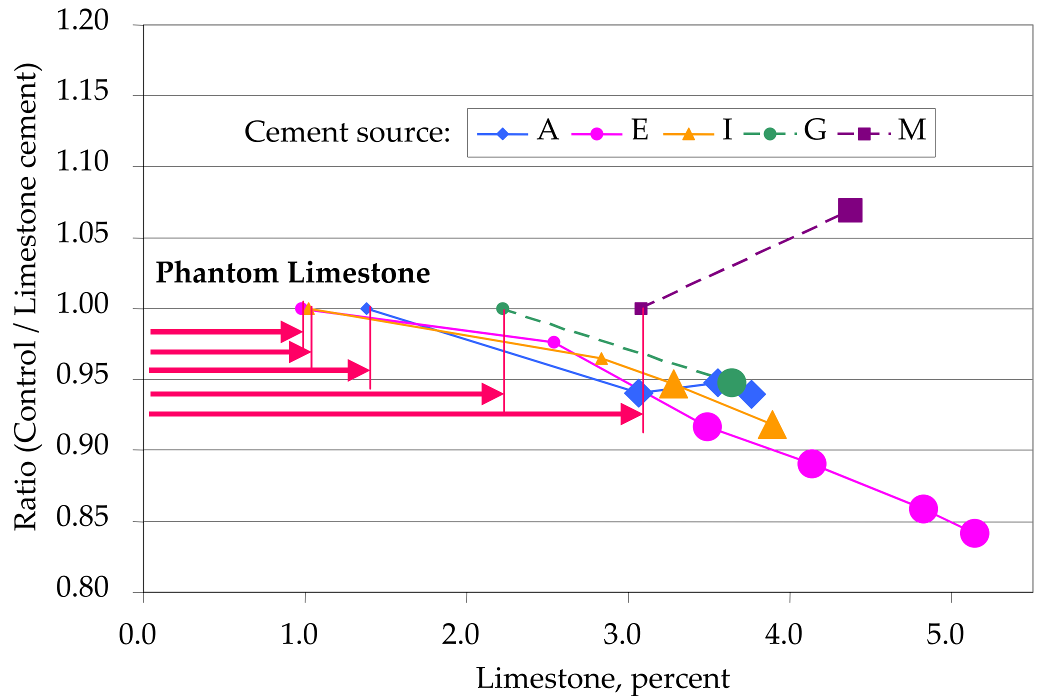

Figure 7. Depiction of "phantom limestone" in interground portland cements. ASTM C 150-determined limestone content is plotted on the x-axis—see Figure 5 for the same plot of actual limestone content vs. drying shrinkage of concretes.

Interim Conclusions

A statistically valid, blind testing program was launched by the California Department of Transportation (Caltrans) in August of 2007 to determine the effect of intergrinding raw limestone into portland cements as currently allowed by the ASTM C 150 portland cement standard. Only California's Type II/V cements were used in this study. A total of five cements were identified and blended with 25 percent fly ash in order to isolate the effect of raw limestone on the durability and long-term performance of concretes used by the State of California in structures and pavements. Three "pillars" of concrete durability and performance were identified and investigated: *strength, shrinkage*, and *permeability*.

Portland cement containing raw limestone conforming to ASTM C 150 performs better than the comparable limestone-free cement from the same source in compressive strength, up to 91 days age, and in electrical conductivity using a rapid chloride penetration test method.

Concrete drying shrinkage increases when raw limestone is included in the cement. The practical impacts, however, are minor and can be addressed by other engineering measures. Caltrans, as well as other agencies, has used limits on concrete drying shrinkage in cases where it was believed to be important. It may be appropriate to consider drying shrinkage as a key parameter in a performance-based specification in lieu of limiting limestone content at a different level than those currently allowed under the ASTM C 150 standard specification.

Restrained drying shrinkage tests have not yet been completed. The restrained drying shrinkage test results may shed more light on a mixture's propensity to prematurely crack due to drying shrinkage. However, insufficient data exist at this time to report on the results of the restrained drying shrinkage tests.

Appendix A – Drying Shrinkage of Concrete and Mortars

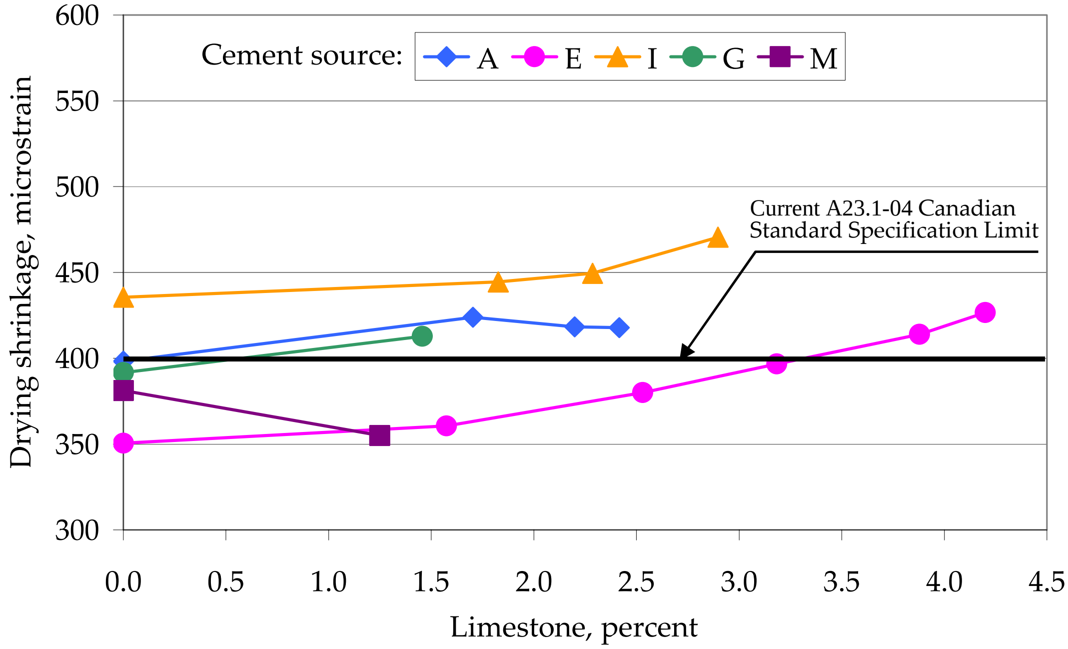

Figure A.1. 28-day concrete drying shrinkage values as a function of cement source and limestone percentage from ASTM Test Method C 157.

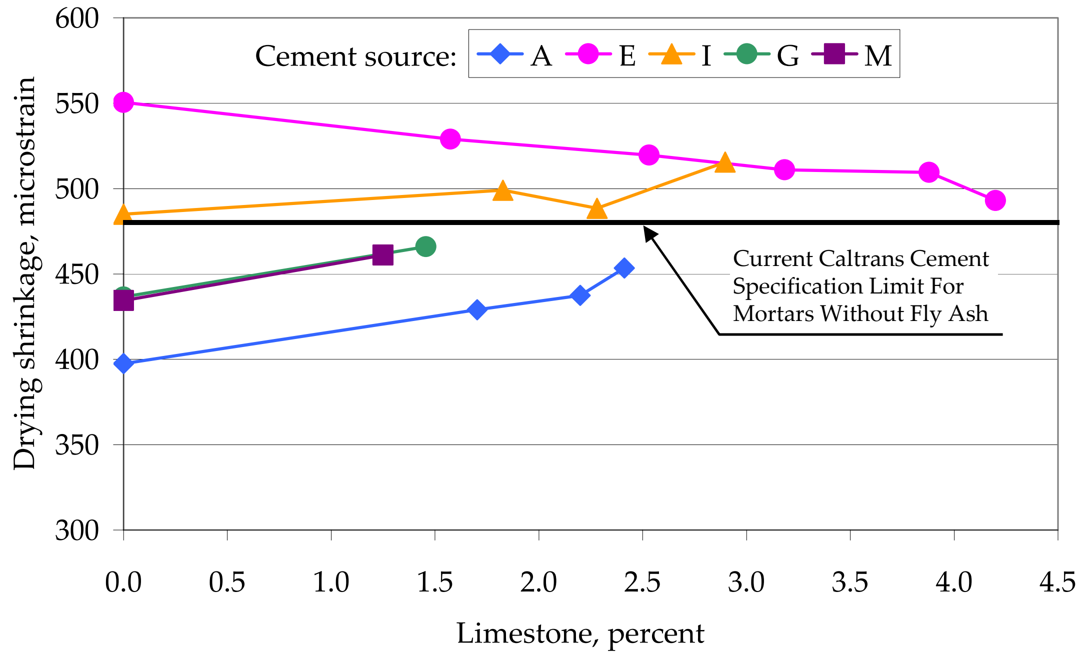

Figure A.2. 4-day mortar drying shrinkage values as a function of cement source and limestone percentage from California Test Method CT 527.

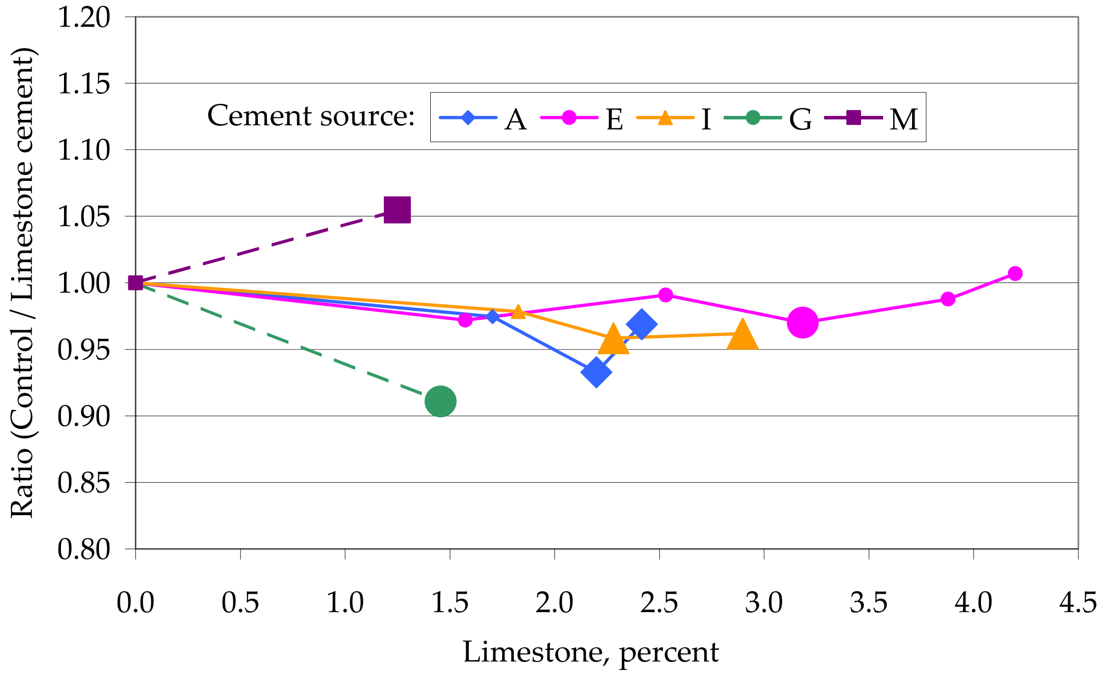

Figure A.3. Shrinkage ratios of mortars with fly ash as a function of cement source and limestone percentage from California Test Method CT 527.

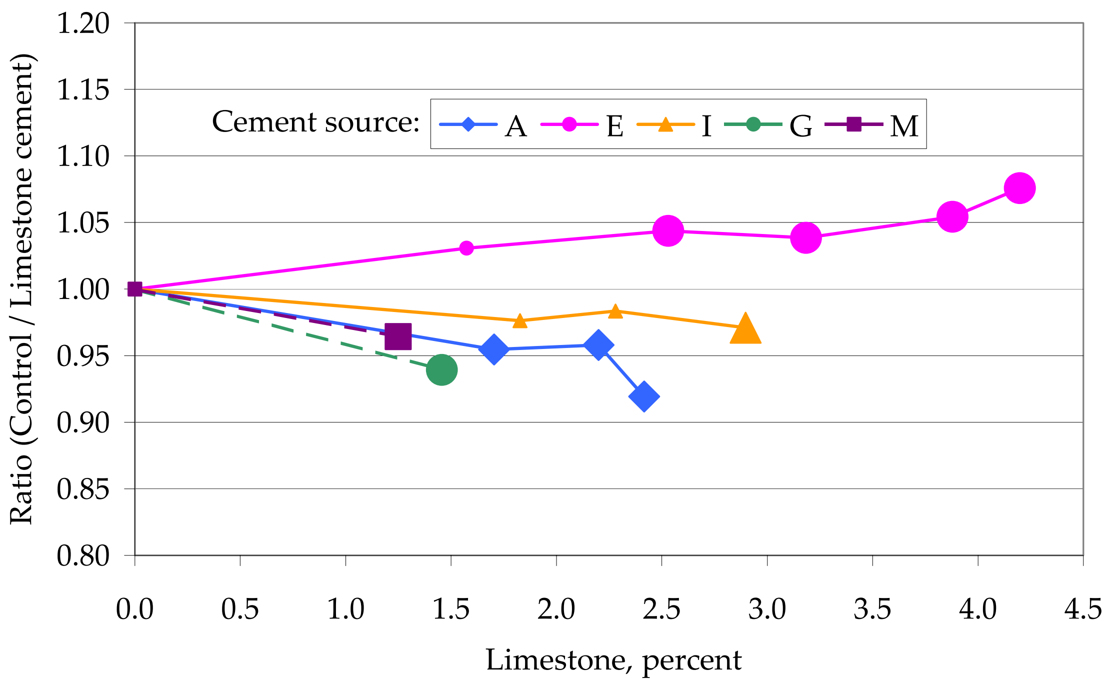

Figure A.4. Shrinkage ratios of mortars without fly ash as a function of cement source and limestone percentage from California Test Method CT 527.

Appendix B – Water/Cementitious Ratio and Flow

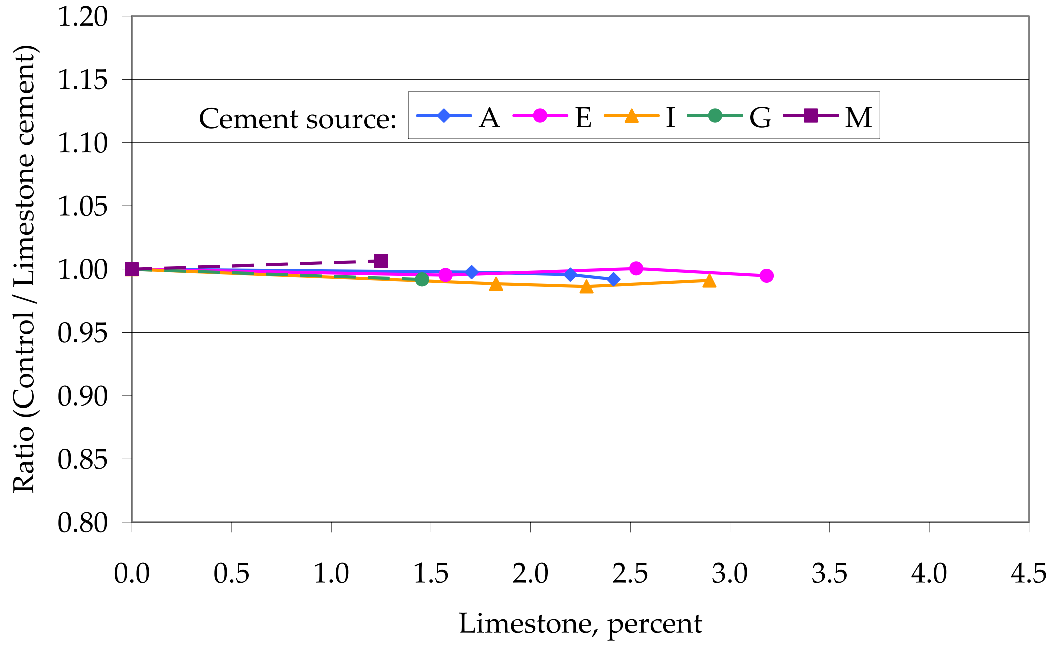

Figure B.1. Water/cementitious ratios as a function of cement source and limestone percentage.

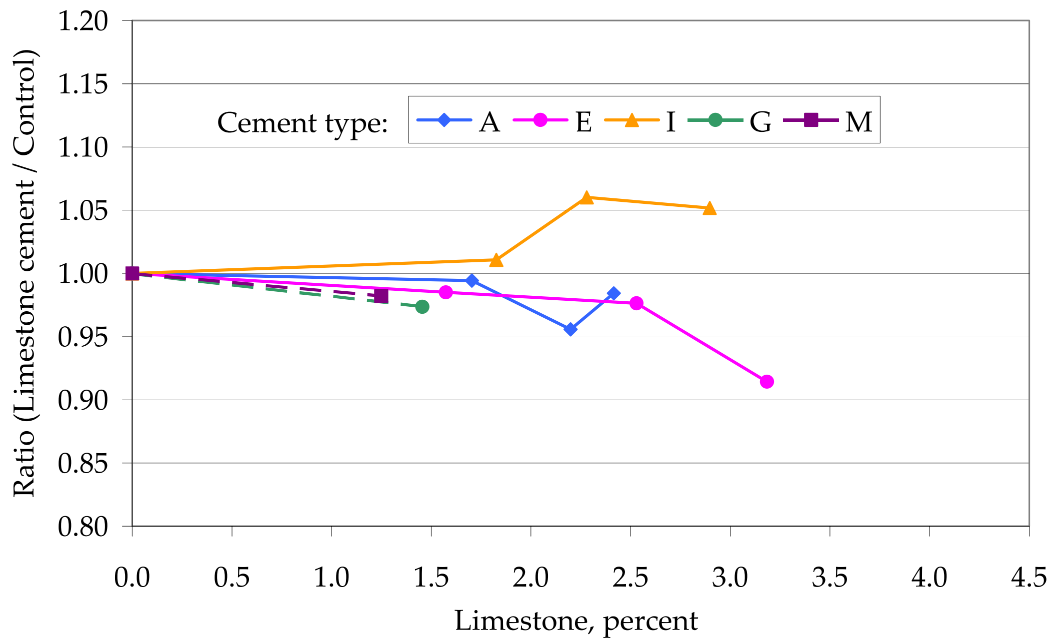

Figure B.2. Flow ratios of mortars with fly ash as a function of cement source and limestone percentage.

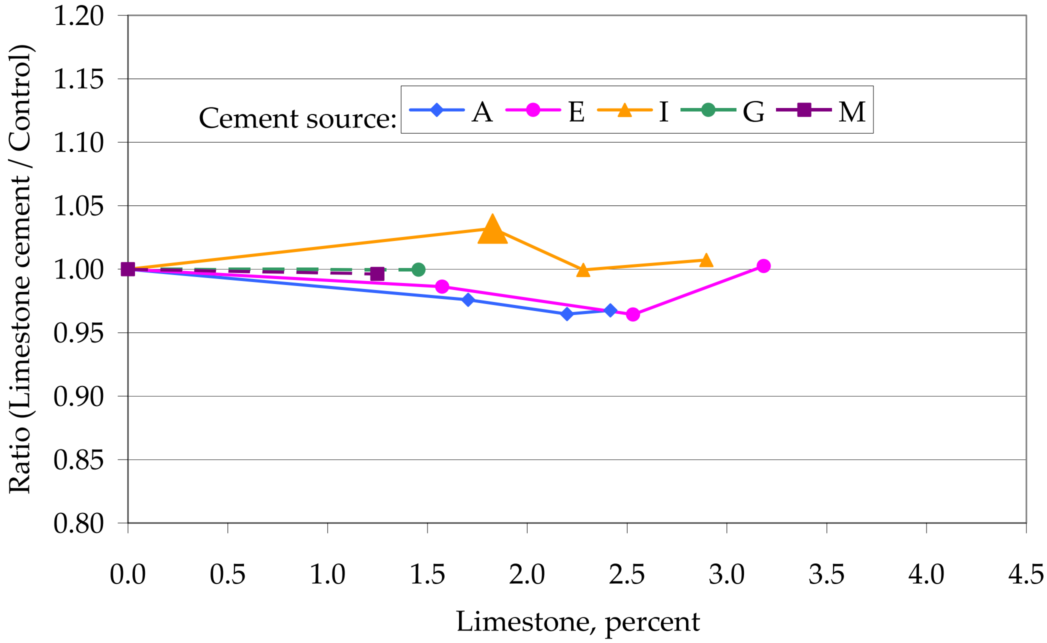

Figure B.3. Flow ratios of mortars without fly ash as a function of cement source and limestone percentage.

Appendix C – Modulus of Elasticity

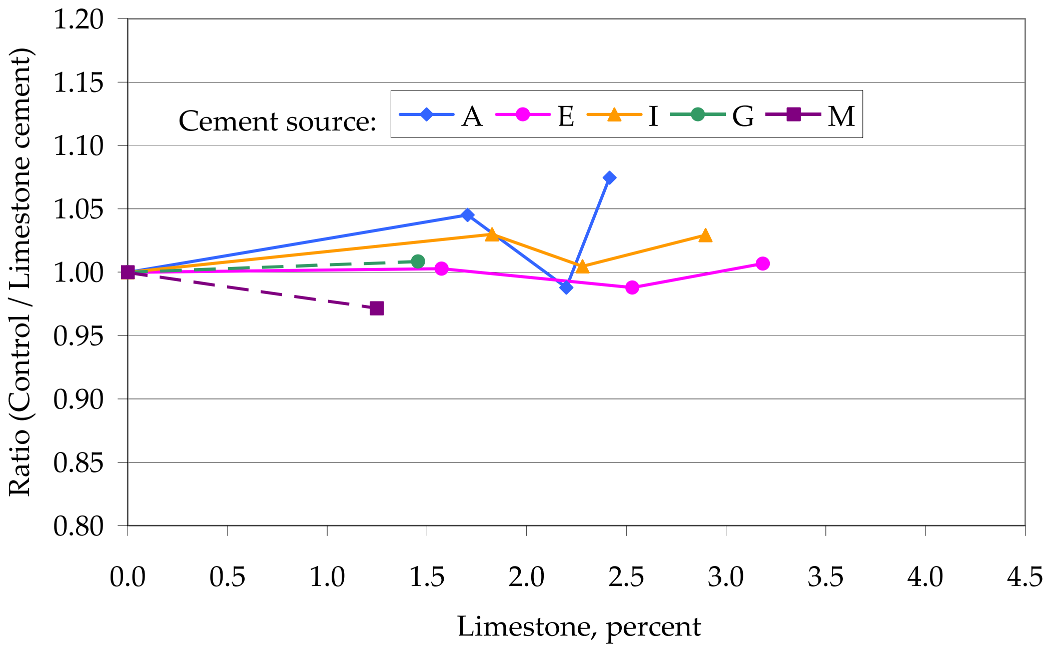

Figure C.1. Modulus of elasticity ratios as a function of cement source and limestone percentage.

Appendix D – Measured Limestone Contents

Table D.1. Target versus actual amounts of limestone

Cement type	Target limestone, percent	Actual limestone, percent	Limestone difference (target - actual), percent
A	1.60	1.70	-0.10
	2.20	2.20	0.00
	2.85	2.42	0.43
E	1.60	1.57	0.03
	2.20	2.53	-0.33
	2.85	3.18	-0.33
	3.50	3.88	-0.38
	4.20	4.20	0.00
I	1.60	1.83	-0.23
	2.20	2.28	-0.08
	2.85	2.90	-0.05
G	1.35	1.46	-0.11
M	2.80	1.25	1.55