

Mitigation of Alkali-Silica Reactivity in New Mexico

by

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15. Abstract Alkali-silica reaction occurs when reactive silica in aggregates chemically reacts with alkaline components of Portland cement forming ASR gel. So long as the internal relative humidity of concrete exceeds 80 percent, the gel absorbs water and swells damaging the concrete. In the summer 1997 the NMSHTD Research Bureau initiated an experiment to develop data for use in specifying methods to eliminate ASR damage in Portland cement concrete. The project was conducted by the Materials Research Center, ATR Institute at the University of New Mexico. The approach was a cooperative effort involving UNM, NMSHTD Research Bureau and Materials Lab Bureau, representatives of industry (FMC Corporation, Western Mobile/La Farge) and researchers from New Mexico Institute of Mining and Technology. Two randomized, full-factorial analysis of variance experiments were designed and conducted to assess the effects of additives (fly ash and lithium nitrate) on expansion due to alkali-silica reaction. Expansion was measured using the Test Method AASHTO T 303 for accelerated testing. Test results were used as a basis for development of guidelines for use in proportioning concrete mixtures that will not exhibit ASR distress in field concrete. The criteria developed during the Strategic Highway Research Program (SHRP) set limits on laboratory measured expansion that correlates with acceptable field performance. This experiment developed quantitative results for New Mexico concrete materials that meet the SHRP criteria. Based on use of the guidelines developed from these tests and the SHRP criteria the research demonstrates ASR can be eliminated in New Mexico. Eliminating ASR will extend the life of concrete structures, such as bridges and pavements, significantly. Based on estimates by the Bridge Design Section, 20 bridges per year are built, 1/2 to 3/4 of these are replacing bridges due to ASR related distress. Using average numbers it is estimated that one rehabilitation and one replacement of the bridge will be eliminated by preventing ASR distress over a 100 year bridge life. Present values are \$0.7 and \$0.4 million for replacement and rehabilitation respectively. Summing these values for 10 to 15 bridges per year produces \$11 to \$16.5 million in annual savings.			
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SI* (MODERN METRIC) CONVERSION FACTORS				
Symbol	When You Know	Multiple By	To Find	Symbol
LENGTH				
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
<u>AREA</u>				
in ²	square inches	645.2	square millimeters	mm ²
ft ²	square feet	0.093	square meters	m ²
yd ²	square yards	0.836	square meters	m ²
ac	acres	0.405	hectares	km ²
mi ²	square miles	2.59	square kilometers	km ²
<u>VOLUME</u>				
fl oz	fluid ounces	29.57	milliliters	ml
gal	gallons	3.785	liters	l
ft ³	cubic feet	0.028	cubic meters	m ³
yd ³	cubic yards	0.765	cubic meters	m ³
NOTE: Volumes greater than 1000 L shall be shown in m ³ .				
<u>MASS</u>				
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams	Mg
<u>TEMPERATURE (exact)</u>				
°F	Fahrenheit temperature	5(F-32)/9 or (F-32)/1.8	Celsius temperature	°C
<u>ILLUMINATION</u>				
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m ²	cd/m ²
<u>FORCES and PRESSURE or STRESS</u>				
lbf	poundforce	4.45	newtons	N
psi	poundforce per square inch	6.89	kilopascals	kPa

*SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.

SI (MODERN METRIC) CONVERSION FACTORS (continued)
APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiple By	To Find	Symbol
<u>LENGTH</u>				
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
<u>AREA</u>				
mm ²	square millimeters	0.0016	square inches	in ²
m ²	square meters	10.764	square feet	ft ²
m ²	square meters	1.195	square yards	yd ²
km ²	hectares	2.47	acres	ac
km ²	square kilometers	0.386	square miles	mi ²
<u>VOLUME</u>				
ml	milliliters	0.034	fluid ounces	fl oz
l	liters	0.264	gallons	gal
m ³	cubic meters	35.71	cubic feet	ft ³
m ³	cubic meters	1.307	cubic yards	yd ³
<u>MASS</u>				
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg	megagrams	1.103	short tons (2000 lb)	T
<u>TEMPERATURE (exact)</u>				
°C	Celsius temperature	1.8C+32	Fahrenheit temperature	°F
<u>ILLUMINATION</u>				
lx	lux	0.0929	foot-candles	fc
cd/m ²	candela/m ²	0.2919	foot-Lamberts	fl
<u>FORCES and PRESSURE or STRESS</u>				
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	psi

(Revised August 1992)

Mitigation of Alkali-Silica Reactivity in New Mexico

Introduction

Alkali-silica reaction (ASR) in Portland cement concrete structures in New Mexico is a well-known problem to highway engineers. The problem causes premature distress in bridge structures and pavements, shortening their life. In a typical example, a bridge structure will require major rehabilitation at 25 years of age and replacement before 50 years of age when affected by ASR distress. Without the influence of ASR the same bridge would be rehabilitated at 50 years and replaced at 80 to 100 years. Using current data it is estimated that eliminating ASR in bridges alone would result in cost savings of \$11 to \$16.5 million per year in current dollars.

Prior to 1970 using low-alkali cement, those with 0.6 percent or less sodium oxide equivalent, was believed to adequately mitigate ASR in concrete. In the mid 1970s, seven year old concrete pavement on Interstate Highway 40 in Albuquerque showed significant deterioration. The Portland Cement Association diagnosed the distress as the result of ASR. The solution recommended and implemented since that time (the last 20+ years) was to introduce fly ash as a partial cement replacement to further reduce available alkali content in concrete mixes. Experience since the mid 1970s has shown that many concrete bridge decks, structures and pavements require major rehabilitation or replacement early in their life cycle due to ASR distress.

The problem was first identified and technically described in 1940 in California (Stanton, 1940). It has been the subject of intense research work since that time. There have been nine international conferences on alkali-silica reactivity in concrete (Anon., 1992). Three books in the literature discuss the ASR problem in detail (Hobbs, 1988; Swamy, 1992; West, 1996). It is known that alkaline components of portland cement chemically react with silica in certain forms found in certain aggregates. The reaction product is referred to as ASR gel. When the relative humidity in the vicinity of the gel exceeds about 80 percent, the gel absorbs water from its surroundings. This water absorption causes swelling that disrupts the structure of surrounding concrete.

In the summer of 1997 the New Mexico State Highway and Transportation Department (NMSHTD) initiated a research project to conduct experiments to ascertain the level and type of additives required to reduce expansion to acceptable levels based on field performance of

concrete facilities. Fly ash, obtained from the combustion of coal, and lithium nitrate were investigated as additives for use in reducing ASR. Acceptability was judged by comparing expansion measured at 14 days of age in AASHTO T 303-96, Standard Method of Test for Accelerated Detection of Potentially Deleterious Expansion of Mortar Bars Due to Alkali-Silica Reaction, to a criteria of 0.1 percent. NMSHTD adopted this criteria based on correlations with acceptable field performance of concrete structures established in the Strategic Highway Research Program (SHRP) (Stark, et. al., 1993).

The work was conducted at the ATR Institute, University of New Mexico (ATRI) and the Research Bureau, NMSHTD. The NMSHTD, Materials Lab Bureau, New Mexico Institute of Mining and Technology, FMC Corporation, Western Mobile/La Farge, Resource Materials Incorporated, and Professor Clifford Qualls, University of New Mexico all made significant contributions and provided support. Rio Grande Portland Cement, Inc., Panhandle Fly Ash, Boral Industries, American Fly Ash, and Phoenix Cement provided materials. Recommendations resulting from this work do not consider all aspects of concrete mixture design, performance and properties, the recommendations specifically address ASR mitigation. Other reactions reported in the technical literature such as alkali-silicate, alkali-carbonate and other alkali-aggregate reactions (West, 1996) are not considered here.

Materials

Five aggregates, five fly ashes, lithium nitrate solution (Lifetime NTM) and a single type I-II low-alkali cement were used in the experiment. Aggregates are described in Table 1. The selection of aggregates was made based on obtaining a range of expansion potential from very high to innocuous. Previous experience and expansion measured in accelerated tests performed by the NMSHTD Materials Lab Bureau were used in selecting these aggregates. Table 2 shows chemical composition data for the aggregates tested. Table 2 reveals large differences in SiO₂, Al₂O₃, CaO and loss on ignition (LOI). The Shakespeare aggregate, referred to here and in the technical literature as Albuquerque, has been used around the world for experiments on ASR because it is a highly reactive aggregate.

Table 1. Aggregate Sources Used in the Experiment

Name	Symbol	Pit-Location	Rock Type	% Exp. ¹	Previous
<u>Experience</u>					
Placitas	PL	Bernalillo	Sand and Gravel	1.34	High-reactivity
Shakespeare	AL	Albuquerque	Sand and Gravel	1.11	High-reactivity
Mimbres	MI	Deming	Sand and Gravel	0.52	Moderate reactivity
Santa Ana	SA	Bernalillo	Sand and Gravel	0.25	Moderate reactivity
Tinaja	TI	Grants	Quarried Limestone	0.00	Innocuous

¹Tests by NMSHTD Materials Lab Bureau using AASHTO TP14, Edition 1A, August 1993 (same as T303 except for editorial changes), Barela (1997).

Table 2. Aggregate Chemical Composition²

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO.	MgO	Na ₂ O	K ₂ O	LOI
Placitas	79.93	9.43	2.54	1.77	0.51	0.96	2.18	1.04
Albuquerque	83.81	7.22	1.75	1.72	0.38	1.35	1.60	1.08
Mimbres	67.01	14.49	4.22	3.49	1.46	3.51	3.15	1.52
Santa Ana	45.93	2.98	0.78	27.01	0.42	0.91	0.48	21.18
Tinaja	3.00	0.30	0.10	53.00	2.00	0.00	0.04	42.58

²New Mexico Institute of Mining and Technology, Socorro, New Mexico (XRF spectrometer)

Fly ash materials and the cement are described are in Table 3. Composition data are shown in Table 4. Fly ash materials are specified in ASTM C 618, Standard Specification for Coal Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete Mixes. These data indicate that the Class F (EF, CF and 4F) ashes and the C/F blend (ET) all meet current C 618 requirements for Class F fly ash. The Class C (TC) ash meets the C 618 Class C requirements. A limited amount of testing was completed using Durapoz™, a calcined clay additive that meets the Class N requirements. This material has not been used in the concrete industry in New Mexico. Large differences in compositions are the sum of oxides, lime (CaO) and magnesium oxide (MgO). The new NMSHTD specification (draft) limits CaO content to 10 percent maximum for fly ash used in portland cement concrete. Cement was from a single lot produced at the Tijeras Canyon Plant operated by Rio Grande Portland Cement Company, Inc., in Albuquerque. As shown in Table 4 the equivalent alkali content is 0.55,

which is less than 0.6 normally considered to be low alkali cement. These are the commercially available ash and cement sources used on most NMSHTD projects. Symbols shown were used throughout this report.

Table 3. Fly Ash and Cement Descriptions/Sources

Symbol	Name (ASTM Class)	Supplier	Source Location
TC	Tolk-(C)	Panhandle Fly Ash	Muleshoe, TX
CF	Coronado-(F)	Boral Industries	St. Johns, AZ
EF	Escalante-(F)	American Fly Ash	Prewitt, NM
4F	Four Corners-(F)	Phoenix Cement	Farmington, NM
ET	Escalante:Tolk, 50:50 Blend	American/Panhandle	(meets C618 Class F)
CC	Durapoz™(N)	Ash Grove Cement	Kansas City, MO
Cement	Type I-II	Rio Grande Portland Cement	Albuquerque, NM

³ C and F Classes are based on ASTM C 618 requirements

Table 4. Composition of Fly Ash and Cement (Percent)

Component	TC	CF	EF	4F	ET	Cement
SiO ₂	39.04	63.37	61.34	62.56	47.41	21.1
Al ₂ O ₃	19.39	22.26	25.11	25.10	21.45	4.3
Fe ₂ O ₃	4.94	5.34	4.42	4.68	4.82	3.2
Sum of oxides	63.37	90.97	90.87	92.34	73.68	28.6
CaO	24.51	3.6	4.94	2.81	17.56	63.9
MgO	5.36	1.06	1.09	0.81	3.54	2.0
Na ₂ O	1.76	1.71	0.59	1.85	1.00	0.2
K ₂ O	0.49	1.24	1.01	0.83	0.68	0.5
SO ₃	1.1	0.02	0.08	0.00	.077	3.0
Moisture	0.05	0.03	0.03	0.10	0.09	---
Loss on ignition	0.17	0.45	0.34	0.23	0.21	1.2
Alkalis as Na ₂ O	1.04	0.88	0.38	0.72	0.65	0.55

Fly ash tests by Resource Materials, Inc., Clermont, Georgia; Cement tests by Rio Grande Portland Cement Company, Inc., Albuquerque, New Mexico.

Lithium nitrate (LiNO_3) was used in the experiment as an additive to mitigate ASR. FMC Corporation supplied the product with the trade name Lifetime N™. The material is supplied as a nominal 30 percent solution of LiNO_3 in water. The manufacturer's recommended dosage for LiNO_3 equals 0.55 gallon per pound of total alkalis in the cement expressed as sodium equivalent ($\text{Na}_2\text{O}_e = \text{Na}_2\text{O} + 0.658 * \text{K}_2\text{O}$) of the mixture. These experiments involved three dosage rates, 75, 100 and 125 percent of the manufacturer's recommended dosage. This was intended to assess the sensitivity to under and over dosing of the admixture. Adjustments in the mix water were calculated on the basis of $\text{H}_2\text{O}:\text{LiNO}_3$ equal to 70.8:29.2 to compensate for the water portion of the Lifetime N™ mixture which was added to the concrete mix.

Experiment Design

Tests were conducted following procedures in AASHTO T 303, Standard Method of Test for Accelerated Detection of Potentially Deleterious Expansion of Mortar Bars Due to Alkali-Silica Reaction. This test specifies proportioning of the materials and procedures for treatment. Specimens were cast in batches large enough to fabricate four mortar bars 11.25 x 1 x 1 inch from each batch. Three specimens had gage points cast in the ends for length change measurements, the fourth was used for pulse velocity measurements. Following removal from the molds length of each specimen was measured, then they were placed in a water bath at room temperature. The container was then placed in an oven and the temperature raised to 80°C. After 24 hours the length was measured for the zero day reading, then specimens were removed and placed into one normal sodium hydroxide (1 N NaOH) at 80°C for the duration of the testing. The volume of liquid in these containers was 4 times the volume of the specimens in each case. Length readings were taken using a comparator with a digital dial gage with a resolution of 0.0001 inch. Measurements made were an initial and at 0, 1, 3, 7, and 14 days in accordance with T 303. Additional measurements not required by T 303 were made at 28 and 56 days at which time the specimens were removed from the ovens and stored, still in the NaOH solution, at the ambient laboratory temperature.

Mix proportions are illustrated in Table 5 for the specimens tested. These proportions represent a single mix that was used to prepare four mortar bars. The water/cement ratio was computed as water to total cementitious material and was held constant at 0.5 in accordance with AASHTO T 303. About 75 percent of each mix was used to fabricate four specimens and the rest was wasted. Three bars were used for expansion measurements and one was used for pulse velocity and mass measurements.

Table 5. Mortar Bar Mix Proportions Used in the Experiment

Material	Control		12 % Ash		24 % Ash		36 % Ash	
	w/o Li	w/Li	w/o Li	w/Li	w/o Li	w/Li	w/o Li	w/Li
Cement	586.7	586.7	516.3	516.3	445.9	445.9	375.5	375.5
Aggregate #8	132.0	132.0	132.0	132.0	132.0	132.0	132.0	132.0
Aggregate #16	330.0	330.0	330.0	330.0	330.0	330.0	330.0	330.0
Aggregate #30	330.0	330.0	330.0	330.0	330.0	330.0	330.0	330.0
Aggregate #50	330.0	330.0	330.0	330.0	330.0	330.0	330.0	330.0
Aggregate #100	198.0	198.0	198.0	198.0	198.0	198.0	198.0	198.0
Water	293.3	261.5*	293.3	261.5*	293.3	261.5*	293.3	261.5*
Flyash	0.0	0.0	70.4	70.4	140.8	140.8	211.2	211.2
LiNO ₃	0.0	44.9	0.0	44.9	0.0	44.9	0.0	44.9
water/cement	0.5	0.5	0.57	0.57	0.66	0.66	0.78	0.78

*Water adjusted for water in the Lifetime NTM admixture, Li mix proportions are for 100 percent of mfg. dose.

The experiment design was based on varying several factors. Two separate experiments were designed, Matrix I, the ash matrix, contained 80 cells and Matrix II, the lithium matrix, had 41 cells. Matrix I was a randomized, full-factorial analysis of variance design and involved three effects that were varied: 5 aggregate types, 5 ash types and 4 ash percentages. Matrix II was a randomized, full-factorial analysis of variance design that involved: 3 aggregate types, 3 lithium nitrate doses and 4 percentages of 4F ash. The TI and SA aggregates were not used in Matrix II to reduce the total effort for the experiment. In each cell of these experiments three repetitions were performed. A set of control specimens was included in each matrix. Tables 6 and 7 illustrate the designs for Matrix I and II. The limited number of tests performed with calcined clay were not part of the randomized experiment design, since only a few tests were possible. AASHTO T 303 procedures were followed through the 14-day readings, then additional readings were made at 28 and 56 days.

Table 6. Matrix I Design—Ash Matrix

Aggregate		TI	SA	MI	AL	PL
Additive	Ash, %					
Control	0	TI-CT	SA-CT	MI-CT	AL-CT	PL-CT
EF	12	TI-EF-12	SA-EF-12	MI-EF-12	AL-EF-12	PL-EF-12
	24	TI-EF-24	SA-EF-24	MI-EF-24	AL-EF-24	PL-EF-24
	36	TI-EF-36	SA-CF-36	MI-CF-36	AL-CF-36	PL-CF-36
CF	12	TI-CF-12	SA-CF-12	MI-CF-12	AL-CF-12	PL-CF-12
	24	TI-CF-24	SA-CF-24	MI-CF-24	AL-CF-24	PL-CF-24
	36	TI-CF-36	SA-CF-36	MI-CF-36	AL-CF-36	PL-CF-36
4F	12	TI-4F-12	SA-4F-12	MI-4F-12	AL-4F-12	PL-4F-12
	24	TI-4F-24	SA-4F-24	MI-4F-24	AL-4F-24	PL-4F-24
	36	TI-4F-36	SA-4F-36	MI-4F-36	AL-4F-36	PL-4F-36
TC	12	TI-TC-12	SA-TC-12	MI-TC-12	AL-TC-12	PL-TC-12
	24	TI-TC-24	SA-TC-24	MI-TC-24	AL-TC-24	PL-TC-24
	36	TI-TC-36	SA-TC-36	MI-TC-36	AL-TC-36	PL-TC-36
ET	12	TI-ET-12	SA-ET-12	MI-ET-12	AL-ET-12	PL-ET-12
	24	TI-ET-24	SA-ET-24	MI-ET-24	AL-ET-24	PL-ET-24
	36	TI-ET-36	SA-ET-36	MI-ET-36	AL-ET-36	PL-ET-36

Table 7. Matrix II Design—Lithium Matrix

Aggregate		TI	SA	MI	AL	PL
Additive	LiNO ₃ , %					
Control	0	TI-CT-R1	SA-CT-R1	MI-CT-R1	AL-CT-R1	PL-CT-R1
Li + 0% 4F Ash	75			MI-L00-75	AL-L00-75	PL-L00-75
	100			MI-L00-100	AL-L00-100	PL-L00-100
	125			MI-L00-125	AL-L00-125	PL-L00-125
Li + 12% 4F Ash	75			MI-L12-75	AL-L12-75	PL-L12-75
	100			MI-L12-100	AL-L12-100	PL-L12-100
	125			MI-L12-125	AL-L12-125	PL-L12-125
Li + 24% 4F Ash	75			MI-L24-75	AL-L24-75	PL-L24-75
	100			MI-L24-100	AL-L24-100	PL-L24-100
	125			MI-L24-125	AL-L24-125	PL-L24-125
Li + 36% 4F Ash	75			MI-L36-75	AL-L36-75	PL-L36-75
	100			MI-L36-100	AL-L36-100	PL-L36-100
	125			MI-L36-125	AL-L36-125	PL-L36-125

Matrix II was designed using aggregates (PL, AL, MI) the most reactive in Matrix I tests, one Class F ash (4F) at 4 levels (0, 12, 24, 36) and three levels of lithium nitrate (75, 100 and 125). Lithium nitrate was added at the manufacturer's recommended dosage, recommended plus 25 percent and recommended minus 25 percent. A second set of control samples was cast in this matrix. Matrix II was a fully randomized, full-factorial analysis of variance experiment containing 41 cells. Each cell was made up of four mortar bars as described above. During planning for these tests there was concern about the possible leaching of lithium while samples were submerged in solutions. To evaluate this aspect chemical analysis of the initial soak water and the NaOH solution after 14 days were made to determine quantitatively the extent to which Li ion was leached out of mortar bars while they were submerged.

Results

Control specimens

Aggregate selections were made on the basis of previous NMSHTD tests. The five aggregates selected represented a range of reactivity from very high to innocuous (no expansion). Expansion measurements on control samples (no additives) for these five aggregates are shown plotted versus time in Figure 1. Each data point plotted is the mean of three measurements. There were two sets of control specimens for each aggregate tested. The NMSHTD acceptance criteria is 0.1 percent at 14 days.

The magnitude of expansion for PL and AL samples was 0.8 percent at 14 days. Subsequent measurements at 28 and 56 days are different with PL exhibiting somewhat more expansion than AL. The MI and SA aggregates also were very near the same value, about 0.5 percent at 14 days, with the MI aggregate exhibiting greater expansion at later times. The TI aggregate was innocuous in these tests and exhibited negligible expansion at all times. Previous test results obtained by NMSHTD are shown in Table 1. The AASHTO precision statement indicates that two tests by different laboratories on the same aggregate should not differ by more than 27 percent of their mean. Based on this precision statement, aggregates tested in this experiment from sources that were previously tested by NMSHTD are not the same. This means there is significant variability within sources. The implications of this within source variability must be considered in formulating specifications and testing requirements.

It is apparent in Figure 1 that following the initial steep expansion-time curve there is a break, which occurred earlier for MI and SA and later for PL and AL producing a large difference at 14 days. In all of the reactive aggregate samples the slope of expansion versus time

decreased from 7 to 14 days in comparison with earlier data. Then from 14 to 28 days all reactive aggregate samples exhibited increases in the slope. Following the 28 day readings the slope of all samples shown in Figure 1 do not greatly differ. The present state-of-the-art does not offer adequate theory to explain this expansion behavior.

ASTM C 1260, Standard Test Method for Potential Alkali Reactivity of Aggregate (Mortar- Bar Method) states, “Because the specimens are exposed to a NaOH solution, the alkali content of the cement is not a significant factor in affecting expansion.” As discussed below, in the present experiment it is clear the composition of the cementitious material (cement plus fly ash) has a dramatic effect on expansion of the mortar bars.

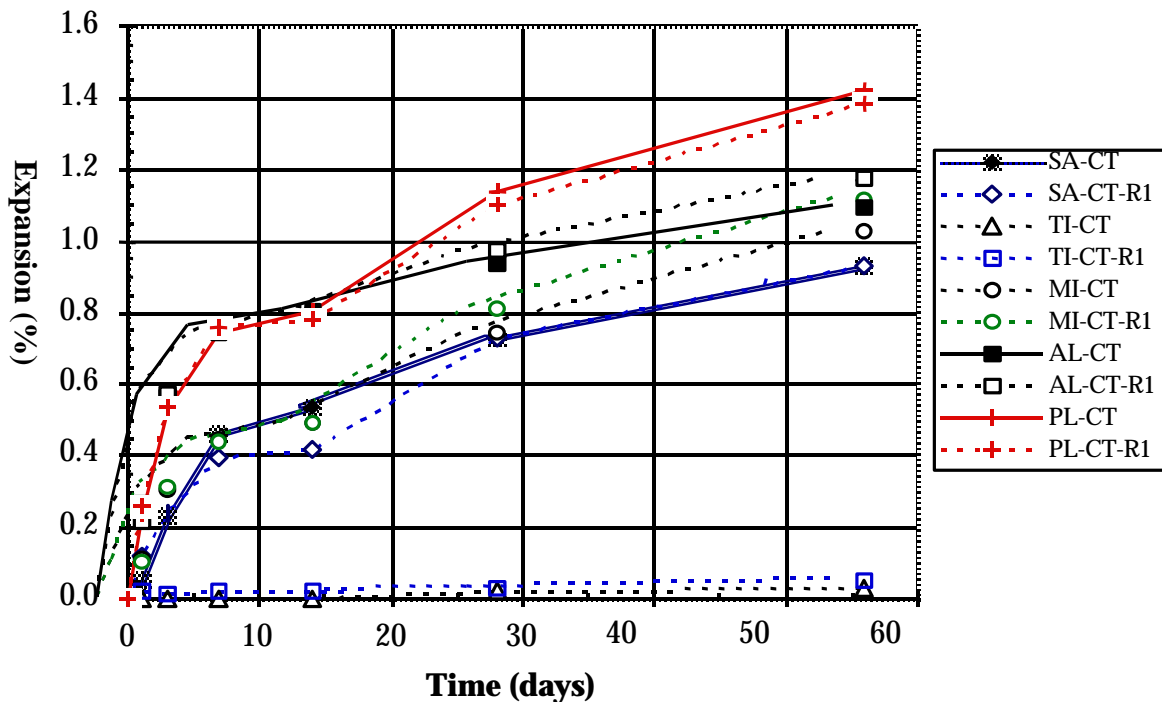


Figure 1. Expansion-Time Data for Control Specimens

Effect of fly ash additives in mitigating expansion

Expansion data for mortar bars made with all five fly ash materials used in the experiment are shown in Figures 2 through 6 using the five aggregates tested. The figures show 14 day expansion measured in the T 303 test plotted versus the fly ash percent by weight of total cementitious material (cement plus additive). For example, 24 percent means that 24 percent by

mass of cement plus fly ash total is fly ash. These values were shown previously in Table 5. The criteria used for acceptance by NMSHTD is 0.1 percent expansion at 14 days.

Figure 2 shows data for Santa Ana aggregate mixes. All of the Class F fly ashes (EF, CF, 4F) at 24 and 36 percent reduce the mean 14 day expansion below 0.1 percent. The Class C fly ash (TC) does not achieve acceptable reduction. The C/F blend (ET) achieves acceptable reduction of expansion when 36 percent was used in the mix. Based on interpolation, it may be concluded the mean expansion could be controlled with about 20 percent of any of the Class F fly ash additives when used with Santa Ana aggregate. Effectiveness of the Class F ashes based on these data rank as follows, 4F, EF, CF, although the differences are small.

Data for TI in Figure 3 show there was negligible expansion with this aggregate in all tests. This aggregate is innocuous and does not exhibit ASR.

Figure 4 shows data for Mimbres aggregate mixes. All of the Class F fly ashes (EF, CF, 4F) at 24 and 36 percent reduce the mean 14 day expansion to less than 0.1 percent. Again the Class C (TC) ash does not reduce 14 day expansion to the acceptable level at any of the percentages studied. The C/F blend (ET) achieves acceptable reduction at the 36 percent level only. In contrast to tests on Santa Ana aggregate 20 percent Class F fly ash would not achieve the required reduction in 14 day expansion.

Figure 5 shows data for Albuquerque aggregate mixes. This aggregate is more expansive than the previous reactive aggregates (SA and MI). The Class C (TC) and C/F blend (ET) do not achieve acceptable reduction in expansion. The 12 percent level of Class F ashes also does not achieve as much reduction as in the previous tests for SA and MI. The 24 and 36 percent levels of Class F fly ash are effective, although the 24 percent level is borderline. Also shown are limited amounts of data obtained from the Class N, calcined clay additive, designated as CC in Figure 5. The data suggest this additive may be just as effective in reducing expansion as the Class F fly ashes. Since this additive is not presently used in New Mexico, testing was limited.

Figure 6 shows data for Placitas aggregate mixes. Some of the Class F ashes at 24 percent do not reduce the 14 day expansion below the 0.1 percent criteria desired. Only the 4F ash is successful at 24 percent for Placitas. By interpolating between 24 and 36 percent it is concluded that rates of 25 to 27 percent of Class F fly ashes should achieve acceptable expansion reduction for this aggregate. The Class C (TC) fly ash will not reduce expansion for this aggregate to the acceptable level. The C/F blend (ET) is borderline at the 36 percent level for this aggregate. The relatively high expansion for 24 percent CF appears to be somewhat

anomalous compared to all other data. This was investigated in detail and no explanation was found.

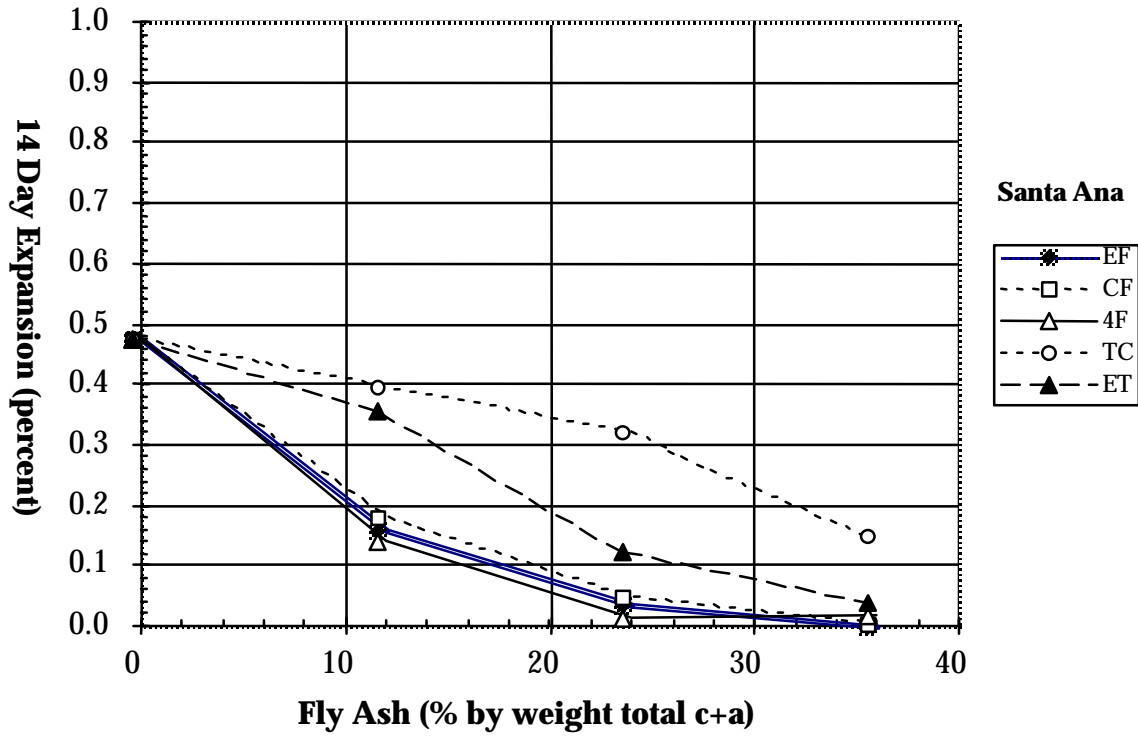


Figure 2. Santa Ana Expansion versus Fly Ash Percent

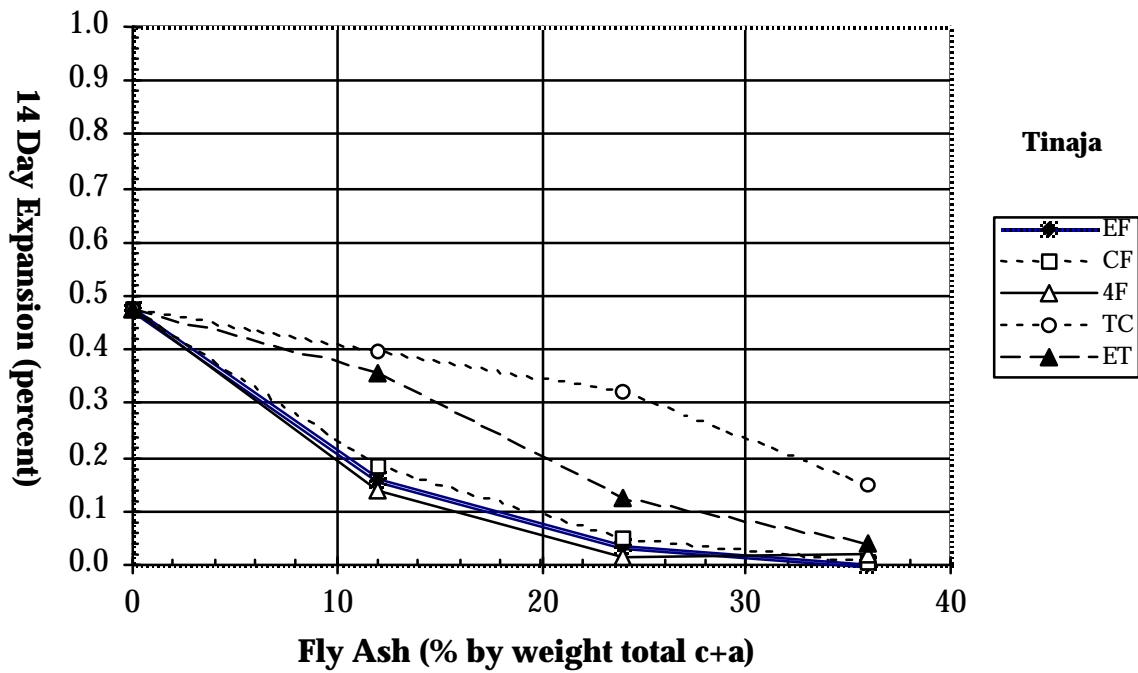


Figure 3. Tinaja Expansion versus Fly Ash Percent

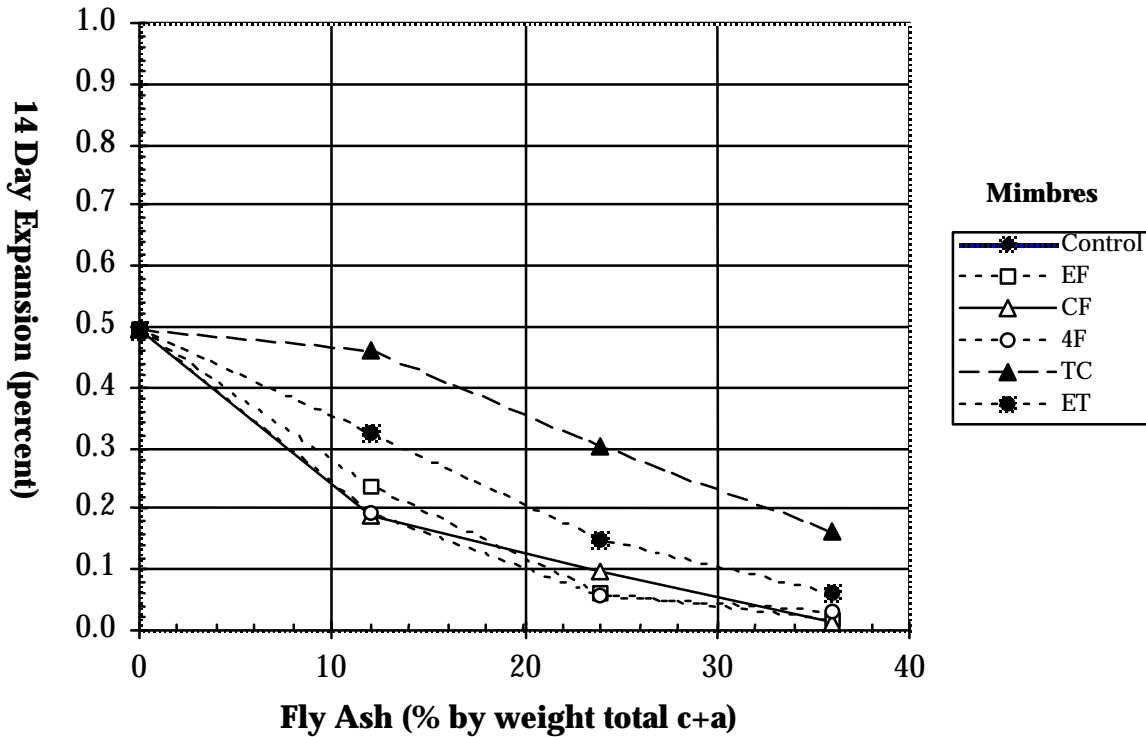


Figure 4. Mimbres Expansion Versus Fly Ash Percent

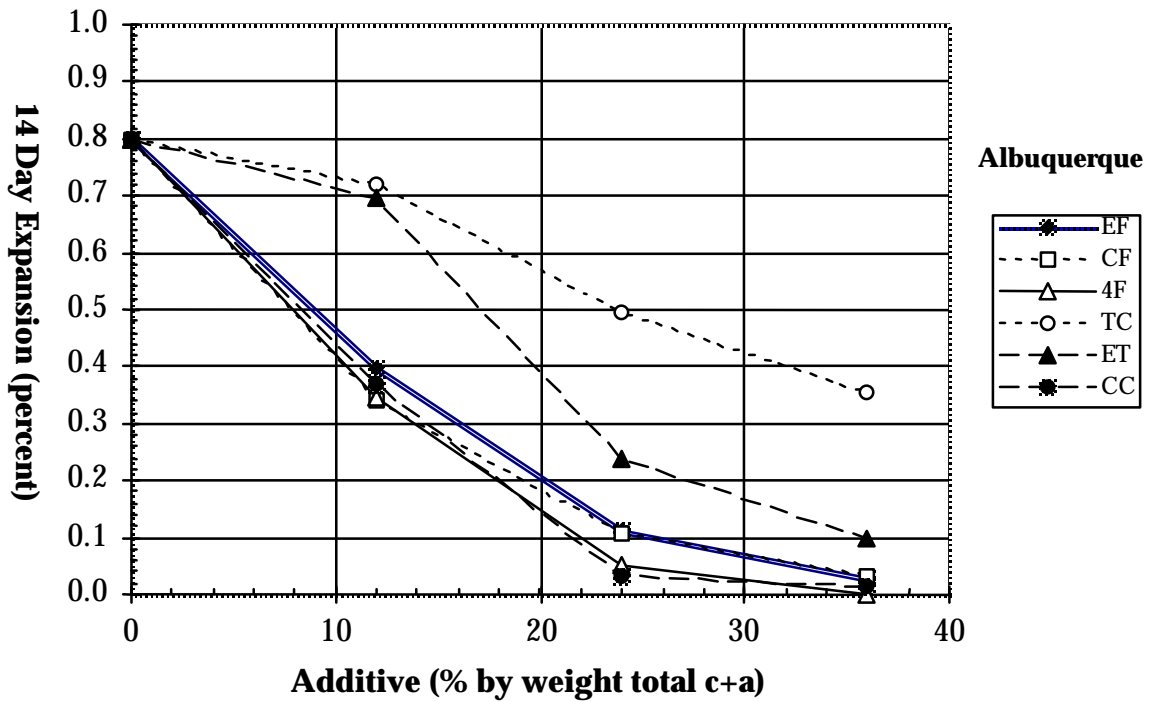


Figure 5. Albuquerque Expansion Versus Fly Ash Percent

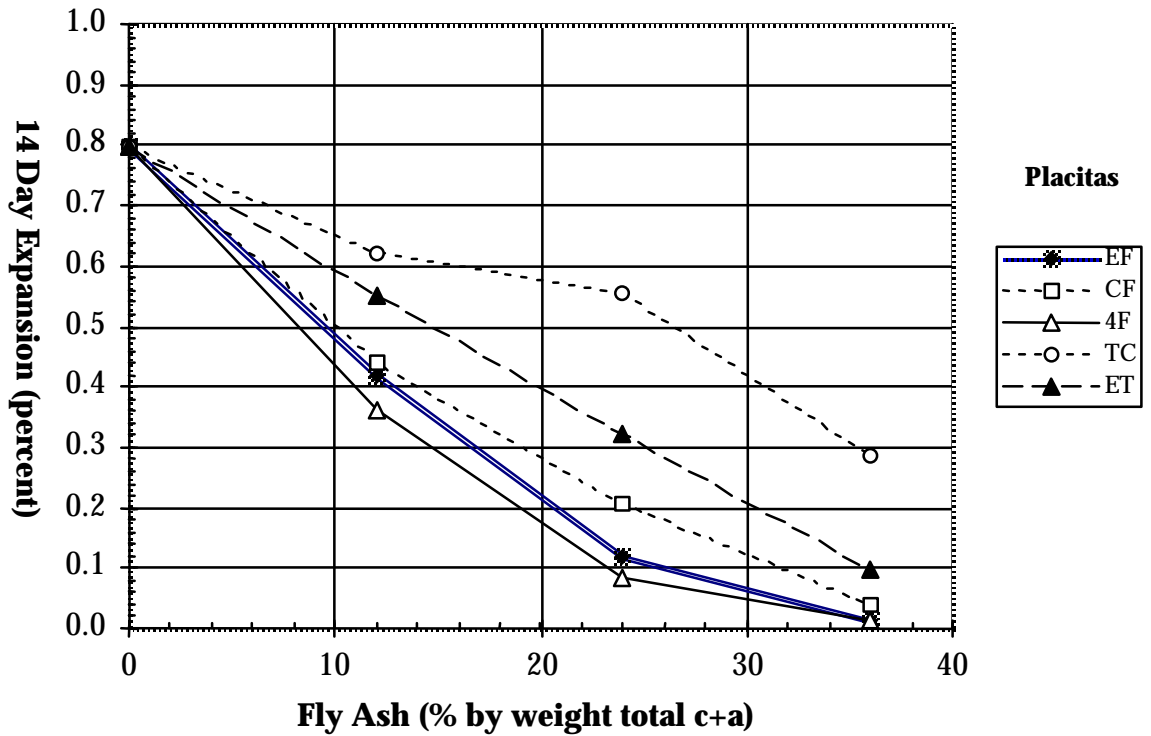


Figure 6. Placitas Expansion Versus Fly Ash Percent

It is clear that the behavior of concrete mixes that utilize Class F fly ash and those using Class C and the C/F blend are different. One goal of this project was to identify compositional characteristics that could be used to specify fly ash composition that would assure adequate reduction in expansion at 14 days. The composition of fly ash makes a significant difference in its influence on expansion due to ASR. Figure 7 shows composition data plotted versus 14 day expansion for AL following a method discussed in the literature (Thomas, 1996). The quantity [alkali + lime]/silica is the amount of equivalent alkali ($\text{Na}_2\text{O} + 0.658 \text{K}_2\text{O}$), plus lime (CaO) divided by the amount of silica (SiO_2) for the total cementitious material (cement plus fly ash). This quantity was computed from the component data shown in Table 4. The computations were made on a weight basis for each component in each mix. Data plotted are for Class F fly ashes only, because the Class C and C/F blend were not effective at the rates used in this experiment. Data for all aggregates show a similar trend, with only the slope of the regression differing. Results from regressions for all reactive aggregates are shown in Table 8. The coefficient of determination (R^2) for these data indicate the quantity [a+l]/s required to reduce the expansion to 0.1 percent is directly related to the reactivity of the aggregate.

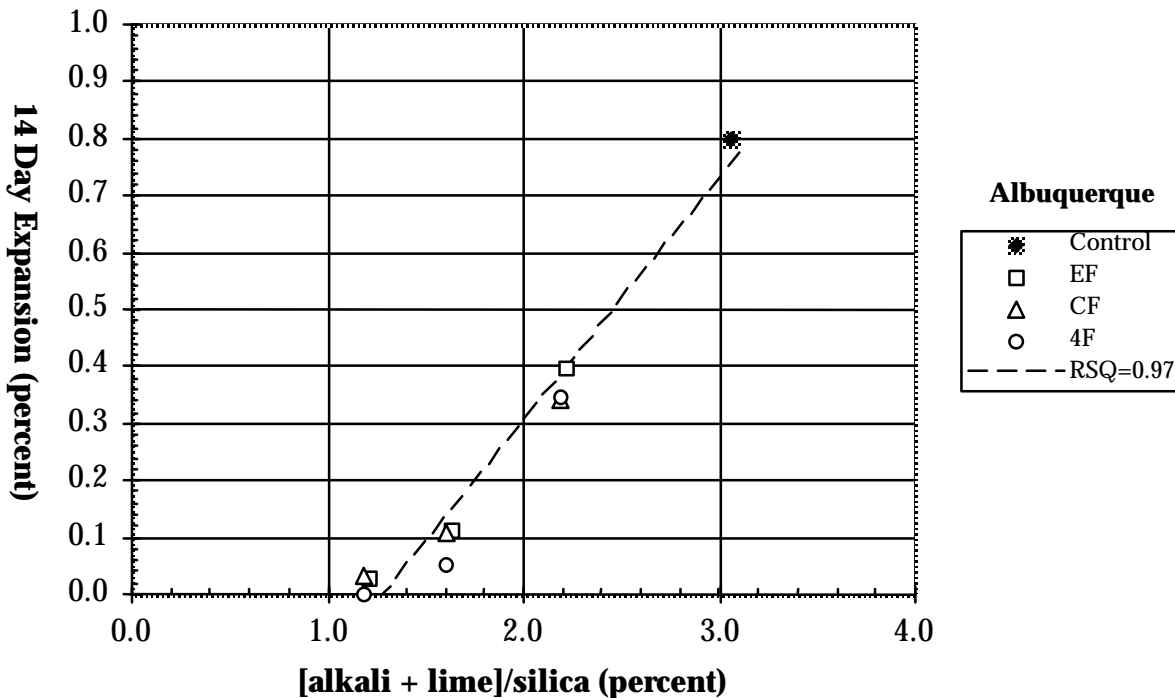


Figure 7. Relation Between Composition and Expansion for Albuquerque

Table 8. Regression Data for Composition of Cementitious Material and Expansion

Aggregate	Expansion	Slope	Intercept	[a+l]/s @ •L = 0.1%	Coefficient of Determination
PL	0.80	0.421	- 0.510	1.45	0.977
Al	0.80	0.426	- 0.542	1.51	0.968
MI	0.49	0.252	- 0.313	1.64	0.957
SA	0.48	0.249	- 0.335	1.75	0.901

Based on the results of T303 testing, the composition of cementitious material (Class F fly ash plus Type I-II cement) required to achieve 0.1 percent expansion may be computed directly. Once a control sample test result is obtained (no additive) the amount of ash required may be computed. These tests involved four specific reactive aggregates and one cement. The conclusions reached should be extended to other materials on the basis of testing with those materials. Another approach that may be considered is setting value of [a+l]/s at 1.45 for all mixes. Based on these data, this would assure expansion mitigation.

Effect of Lithium Nitrate

Tests in Matrix II were conducted using lithium nitrate (LiNO₃) as an additive. Results for mixes made with 75, 100, and 125 percent of the manufacturer’s recommend dosage were obtained. The 14-day expansion measurements are shown in Figures 8 through 10 for the three reactive aggregates tested. The following conclusions were derived from the data. First, LiNO₃ at these dosage rates does not adequately control 14-day expansion based on the 0.1 percent criteria in the T 303 test procedure for these materials. Second, the effect of dosage on expansion varies with different aggregates. The results at 100 and 125 percent of the manufacturer’s recommended dose are equally effective for MI and AL, but for PL the 125 percent dosage is more effective. Third, placing samples into a water bath immediately after removing from molds followed by immersion in 1 N NaOH at 80 °C results in leaching a significant portion of the lithium nitrate from the mortar bars. Actual lithium nitrate content was evaluated by sampling the water after the samples soaked 24 hours and sampling the 1 N NaOH after the 14 day readings. The soak solution samples were then tested for lithium ion concentration. Results of this analysis are presented in Figure 11 that shows 14-day expansion versus the actual lithium content. The sample designations show all specimens contain lithium plus a percentage of 4F fly ash as shown. For example, AL-L24 is Albuquerque aggregate with LiNO₃ and 24 percent 4F fly ash. Data in Figure 11 are all data for LiNO₃ at 75, 100, and 125

percent of the recommended dosage. On average in the T 303 test 43 percent of the LiNO_3 is leached from the specimens. While these tests do not reflect acceptable reductions in expansion, the levels of LiNO_3 are well below the recommended dosage for ASR control. Due to leaching in the T 303 procedure, some other method must be used to fairly evaluate the effect of LiNO_3 on ASR. It is also noted that all samples with fly ash and lithium are below the 0.1 percent criteria except AL at 75 percent LiNO_3 and 12 percent ash, PL at 75 and 100 percent LiNO_3 and 12 percent ash. This is strong evidence that a combination of LiNO and moderate amounts of fly ash will control expansion.

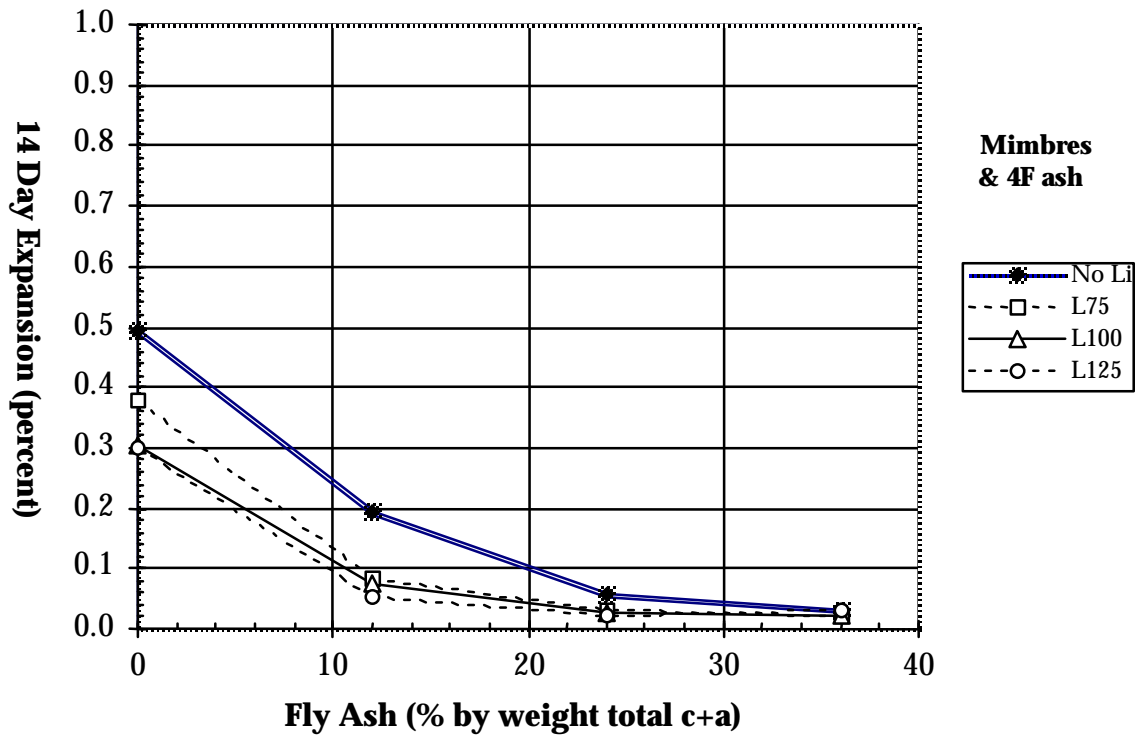


Figure 8. Expansion of Mimbres Samples with Lithium and Fly Ash

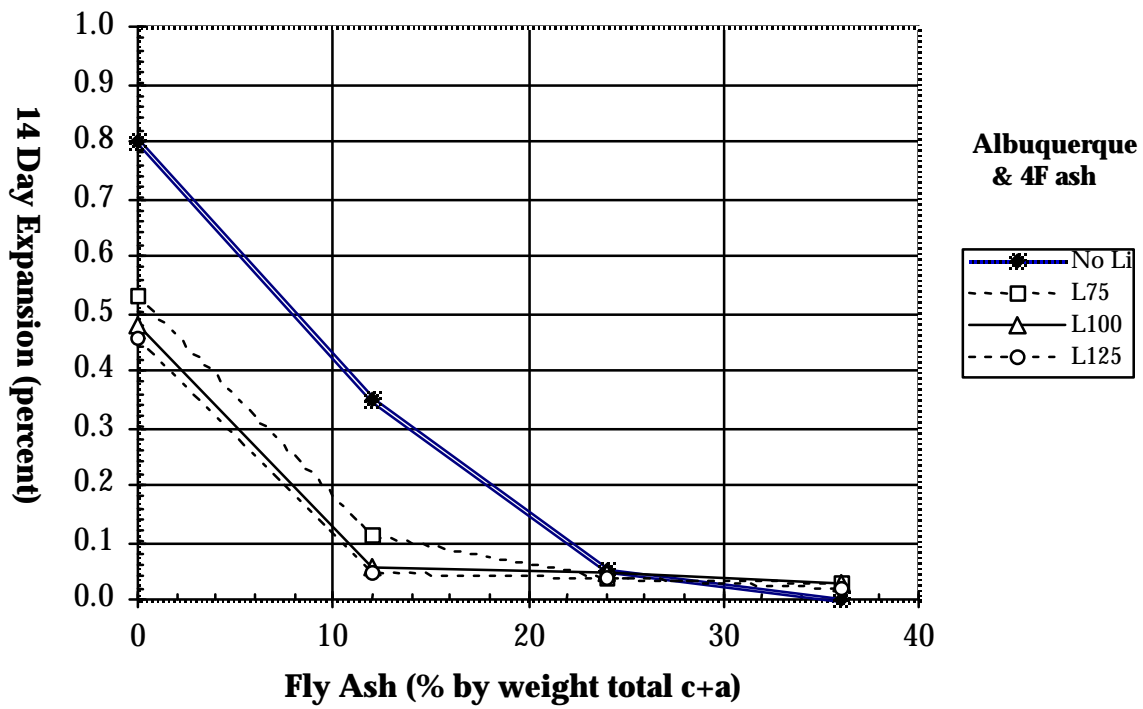


Figure 9. Expansion of Albuquerque Samples with Lithium and Fly Ash

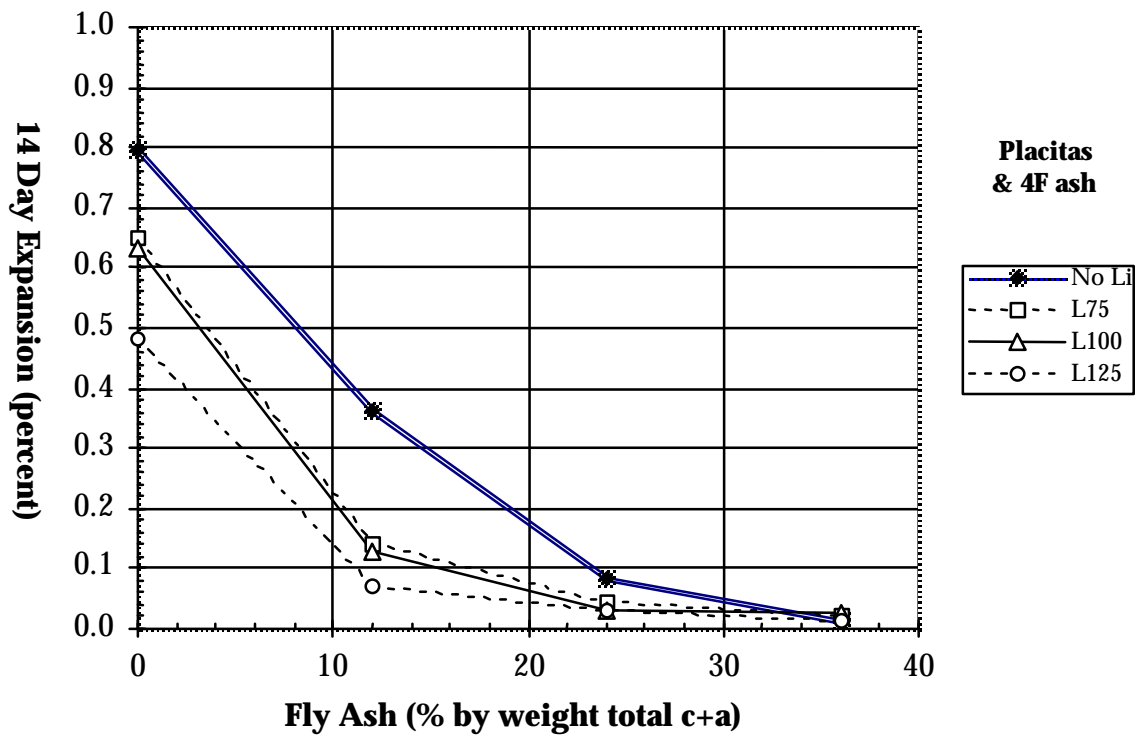


Figure 10. Expansion of Placitas Samples with Lithium and Fly Ash

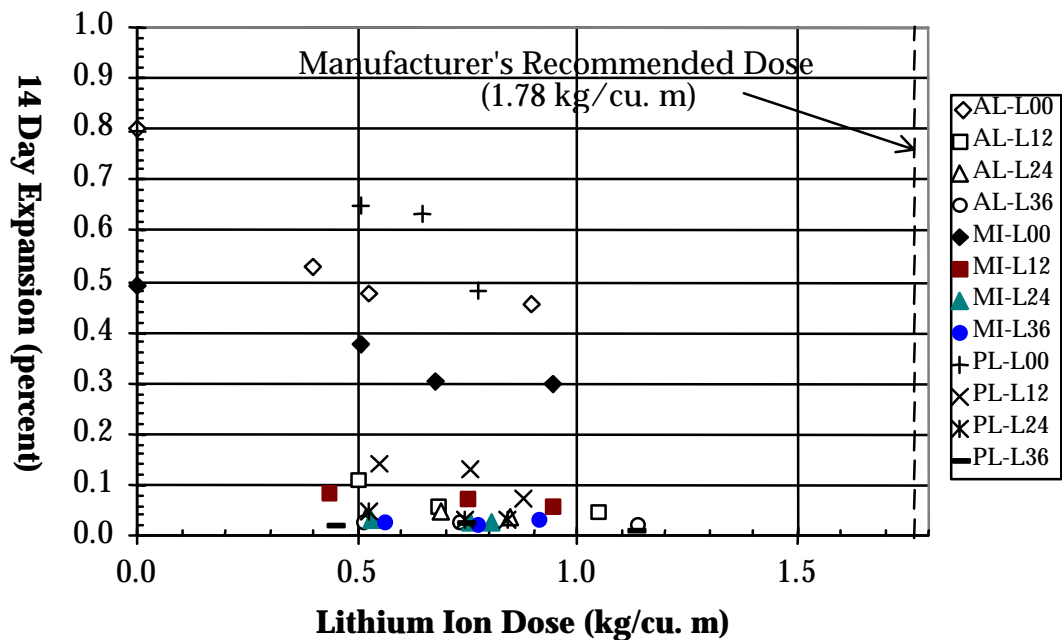


Figure 11. Mortar Bar Expansion versus Actual Lithium Ion Dose

Summary of Statistical Analysis

Analysis of Variance (ANOVA) techniques were used to perform variance components analysis for Matrix I and II. The concept is that the total variance consists of the sum of variance components. The components investigated in this experiment were aggregate type, ash type, ash percent and their interaction terms. Since the TI aggregate exhibited no expansion, the analysis was done with and without TI included. The analysis focused on expansion at 14 days (P14 in the tables below) and average rate of expansion over 56 days (Rate).

Table 9 shows results of variance analysis. The sample to sample variation between the three replicates in any cell is zero. The residual error is also very small which means all effects are statistically significant (P-values < 0.001). Without TI in the computation, aggregate is not very important, which means the other four reactive aggregates behave similarly. With TI in the computation, clearly aggregate becomes a more important source of variance in 14-day expansion. The most important effects in determining percent expansion are the ash type and the percent ash when TI is left out. With TI in the computation, ash type and aggregate become most important, but interaction terms and percent ash are larger sources of variation. These

statistical insights match very well with the observed results obtained from inspection of graphical data previously shown.

Table 9. Variance Components Analysis for Matrix I

Effect	Variance Comp. (w/o TI)		Variance Comp. (w/TI)	
	P14	Rate	P14	Rate
Ash Type	42 %	28 %	27 %	15 %
Percent Ash	38 %	51 %	11 %	28 %
Aggregate	8 %	14 %	21 %	37 %
Aggregate*Percent Ash	5 %	4 %	13 %	12 %
Aggregate*Ash Type	3 %	1 %	11 %	6 %
Ash Type*Percent Ash	3 %	2 %	2%	1 %
Error	1 %	1 %	1 %	1 %
Samples	0 %	0 %	0 %	0 %

From the ANOVA, means may be computed and compared for each effect while the other effects are not considered. Table 10 shows results for means computed for each type ash, percent ash and aggregate. Note that there is a diminishing reduction in 14 day expansion as ash percent is increased. These means illustrate the relative effects very clearly.

Table 10. Analysis of P14 Means form Analysis of Variance

Effect-Ash	Mean P14	Effect-% Ash	Mean P14	Effect -Agg	Mean P14
CT	0.66	00%	0.66	PL	0.31
TC	0.40	12%	0.38	AL	0.30
ET	0.26	24%	0.18	MI	0.18
CF	0.14	36%	0.07	SA	0.16
EF	0.13	—	—	—	—
4F	0.11	—	—	—	—

Conclusions about Effects of Additives

It is concluded that all Class F fly ash additives are effective in controlling ASR expansion measured in this test so long as sufficient fly ash is included in the mix. Figure 12

shows a summary of expansion as percent of control versus fly ash percent. Note that all previous expansion data were plotted as 14 day expansion, while these are percent of control. If the control has an expansion of 0.5 percent, then to achieve 0.1 percent expansion requires a reduction to 0.2 percent of control. Since aggregates may be tested to determine T 303 expansion, this presentation of data is more usable in selecting the required fly ash amount for reducing expansion based on control samples. In this figure, data for Class F fly ash and data for 100 percent of the manufacturer's recommended dose of lithium nitrate in combination with 4F fly ash are shown. The amount of additive required varies with the aggregate and specific fly ash. Based on the testing conducted, a reduction in the range 12.5 to 20 percent of control is required for these New Mexico aggregates.

There appears to be strong evidence that 25 to 27 percent Class F fly ash by weight of total cementitious material is sufficient for most of the aggregates studied. Since these aggregates represent the full range of reactivity, this amount should be adequate for reactive aggregates in New Mexico.

When lithium nitrate is included in the mix, the amount of fly ash required to reduce expansion below 0.1 percent based on the T 303 test is less. It is clear in the T 303 test procedure a significant portion of the lithium is leached out by the soak solutions. This experiment was based on T 303 testing and therefore is it not a fair evaluation of the potential for lithium nitrate to reduce ASR. From these test results a combination of lithium nitrate plus Class F fly ash appears to be a viable combination for mitigating ASR. The specific amounts required must be determined by testing.

Class C fly ash and the blend of Class C and F fly ash do not provide adequate reduction in expansion based on these tests. The new specification being developed by NMSHTD requires no more than 10 percent CaO in fly ash used in any concrete. From Table 4 it is clear the C and C/F blend will not be permitted under this guideline.

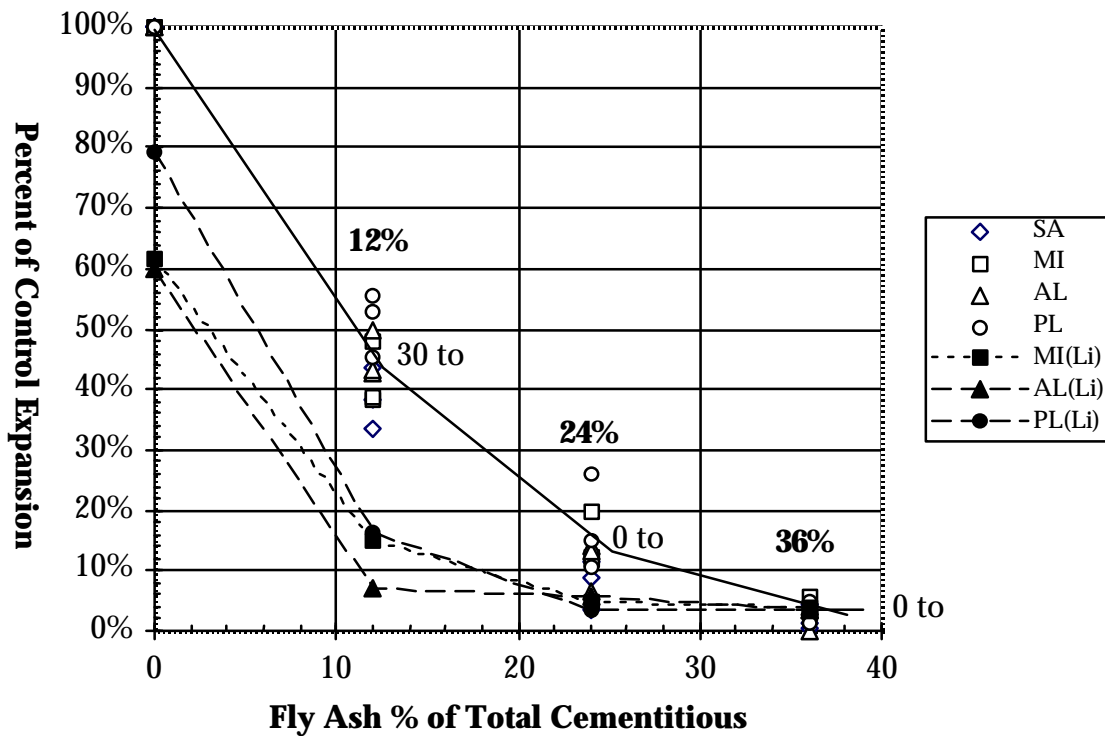


Figure 12. Summary of the Effect of Additives on ASR Expansion

The few tests performed using calcined clay, a Class N pozzolan, indicate that it is as effective as the Class F fly ash materials in controlling expansion. Although this material has not been used in New Mexico, it should be considered a candidate for future use.

Velocity Data

One mortar bar in each cell was tested for pulse velocity and mass during the experiment. The purpose of these tests was to obtain an indicator of stiffness or modulus which in turn is an indicator of strength. Figure 13 is measured pulse travel time plotted versus age. There are two observations regarding these data. First, the innocuous aggregate, TI, is distinct from all others. For the TI samples, travel time decreases initially then stabilizes at about 65 μsec . Lower travel time, indicates higher velocity and therefore higher modulus for this aggregate in comparison to the reactive aggregates which have a travel time of about 85 μsec . All reactive aggregates increase in the period 7 to 14 days followed by some decrease and then a stable travel time. The accelerated test forces the ASR reaction to occur in 14 days which is reflected in increased travel time, decreased velocity and therefore decreased modulus. In these samples the difference between 65 μsec for innocuous to 85 μsec for reactive represents about 6.4 to 3.7 $\times 10^6$ psi (4.5

to 3.5×10^7 kPa) modulus values. These data are an indicator of reduced stiffness in concrete affected by ASR distress. These are significant differences and deserve more study.

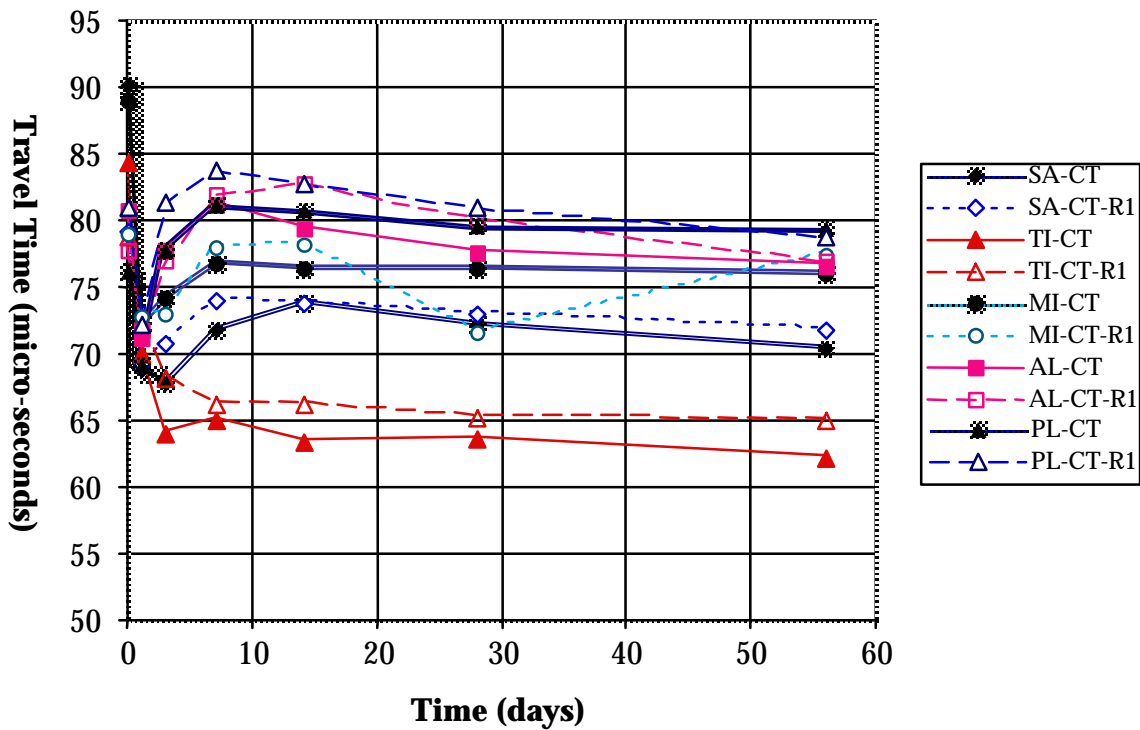


Figure 13. Pulse Travel Time in Control Specimens

In Figures 14 and 15 the travel time measured is plotted versus fly ash percent for mixes using AL and PL aggregates. These data show that reduced expansion attained by using additives also reduces the travel time, indicating higher pulse velocity that indicates higher concrete modulus. These results are consistent with the other data obtained and show that more durable, higher quality concrete is obtained by reducing expansion due to ASR.

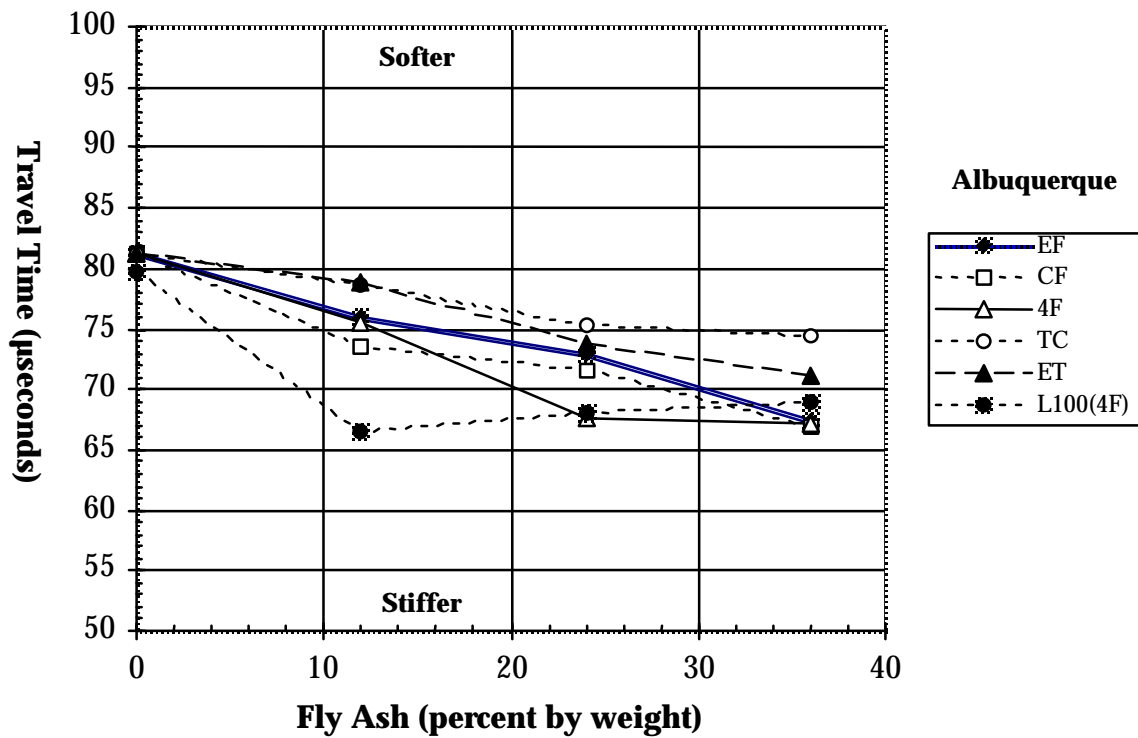


Figure 14. Travel Time Measured for AL Samples

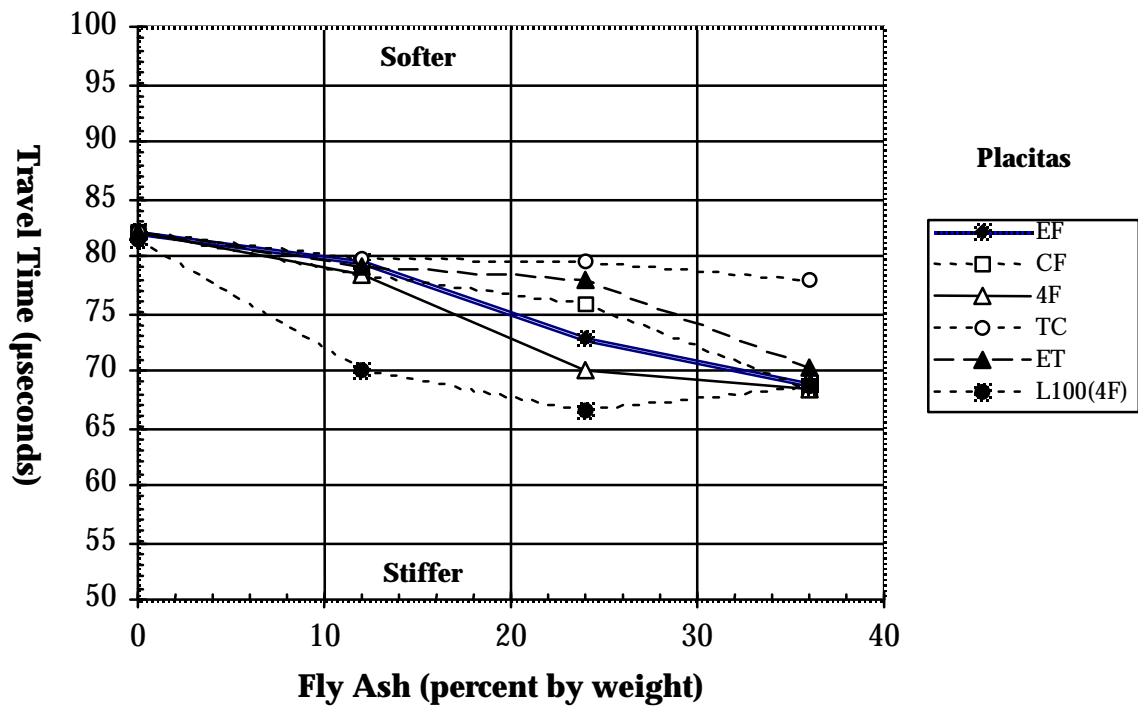


Figure 15. Travel Time Measured for PL Samples

Recommendations for Mitigation of ASR in Concrete Mixes

It is recommended that NMSHTD require a minimum of 25 percent Class F fly ash by weight of total cementitious material for mitigating ASR distress in concrete, unless specific test data based on AASHTO T 303 support another value. An acceptable alternative is a combination of lithium nitrate at the manufacturer's recommended dosage plus Class F fly ash at a minimum of 15 percent by weight of total cementitious material.

The technical literature has presented data demonstrating durability problems with some high fly ash concrete materials (Whiting, 1989). Other physical characteristics must be specified along with the requirement for fly ash additive for concrete mixes to assure durable concrete.

Use of calcined clay has been demonstrated to reduce ASR expansion in a manner similar to Class F fly ash. This should be considered an acceptable alternate and further testing conducted when commercial sources are available in New Mexico.

Research Needs

A method for evaluating the benefit of lithium additions to concrete mixes must be developed that does not leach lithium ion from the concrete mix during testing.

It is essential to develop performance data on structures and pavements in New Mexico to validate the acceptance criteria proposed by SHRP researchers. Work on this should be initiated immediately and will require a long period of monitoring to complete.

There is a critical need to determine how the accelerated test (T 303) relates to actual concrete mixes used in construction. A test is needed that can be performed on production concrete mixes to determine the potential for detrimental expansion.

The impact of fly ash replacement of cement on overall concrete durability is only partly understood. Testing is needed to quantify the effects of fly ash replacement on overall concrete performance and durability and to develop requirements for overall acceptability of concrete.

The chemical and geochemical reactions that are involved in ASR are complex and poorly understood. Some significant advancements have been made in recent years, especially by researchers trying to distinguish various types of reactions and identify those considered detrimental. Further basic research into the mechanisms and reactions is essential to completely understand the phenomena and mitigation measures.

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