EVALUATION OF THE CHEMICAL DURABILITY OF IOWA FLY ASH CONCRETES

PHASE II PROGRESS REPORT

MARCH 31, 1992

IOWA DOT PROJECT HR-327
ERI PROJECT 3295

Sponsored by the Highway Division of the
Iowa Department of Transportation and the
Iowa Highway Research Advisory Board

ENGINEERING RESEARCH INSTITUTE
STATE UNIVERSITY ISU-ERI-AMES 92-408

EVALUATION OF THE CHEMICAL DURABILITY OF IOWA FLY ASH CONCRETES

PHASE II PROGRESS REPORT

MARCH 31, 1992

S. SCHLORHOLTZ
K.L. BERGESON

IOWA DOT PROJECT HR-327
ERI PROJECT 3295
ISU-ERI 92-408

Sponsored by the Highway Division of the
Iowa Department of Transportation and the
Iowa Highway Research Advisory Board

TABLE OF CONTENTS

ABSTRACT iii

INTRODUCTION 1

RESEARCH APPROACH 1

- Sulfate Durability 1
- Alkali Durability 2

CURRENT STATUS 3

- Chemical Tests 3
- Physical Tests 3

RESULTS AND DISCUSSION 4

- Abbreviation Summary 4
- Sulfate Durability Tests 4
- Curing Study 26
- Paste Study 27
- Concrete Study 28
- Alkali Reactivity Tests 36

SUMMARY AND FURTHER DISCUSSION 54

ACKNOWLEDGEMENTS 58

REFERENCES 58

APPENDIX

ABSTRACT

The major objective of this research project is to investigate how fly ash influences the chemical durability of portland cement based materials. The testing program is evaluating how Iowa fly ashes influence the sulfate durability of portland cement-fly ash pastes, mortars, and concretes. Also, alkali-reactivity studies are being conducted on mortar bar specimens prepared in accordance with ASTM C 311.

Preliminary sulfate test results, based only on mortar bar studies, indicate that only the very high-calcium fly ash (29 percent CaO, by weight) consistently reduced the durability of test specimens exposed to a solution containing 5 percent sodium sulfate. The remaining four fly ashes that were used in the study showed negligible to dramatic increases in sulfate resistance. Concrete specimens were only beginning to respond to the sulfate solutions after about one year of exposure; and hence, considerably more time will be needed to assess their performance.

Preliminary results from the alkali-reactivity tests have indicated that the Oreopolis aggregate is not sensitive to alkali attack. However, some of the test results have indicated that the testing procedure may be prone to delayed expansion due to the presence of periclase (MgO) in the Class C fly ashes. Research is being planned to: (1) verify if the periclase is influencing test results; and (2) estimating the magnitude of the potential error.

INTRODUCTION

The following report summarizes research activities conducted on Iowa Department of Transportation Project HR-327, for the period April 1, 1991 through March 31, 1992. The purpose of this research project is to investigate how fly ash influences the chemical durability of portland cement based materials. The goal of this research is to utilize the empirical information obtained from laboratory testing to better estimate the durability of portland cement concrete pavements (with and without fly ash) subjected to chemical attack via the natural environment or the application of deicing salts.

This project is being jointly sponsored by the Iowa Department of Transportation (IDOT) and by the Iowa Fly Ash Affiliate Research group. The research work is also being cooperatively conducted by Iowa State University and Iowa Department of Transportation research personnel. Researchers at Iowa State University are conducting the paste and mortar studies while Iowa Department of Transportation researchers are conducting the concrete study.

RESEARCH APPROACH

A detailed description of the materials and methods used in this study has already been given in a prior report [1]. The purpose of this section is only to give a brief overview of the pertinent details of the experimental program.

Sulfate Durability

Sulfate durability studies were conducted on portland cement-fly ash pastes, mortars and concretes. Three different types (ASTM Type I, I-II and V) of cement and five different fly ash sources were available for use in this study.

Paste specimens were initially molded as $\frac{13}{16}$ inch diameter by 3 inch long cylinders; however, these specimens were deemed unsatisfactory because minor imperfections induced during the molding process degraded faster than the bulk specimen. This caused the expansion versus time relationship to be very erratic. Hence, a new series of paste tests were conducted using 1" x 1" x 11.25" specimens, the Type I cement, and various replacements (0, 15 and 30 percent by weight) of Clinton (Class F) and Council Bluffs (very high-calcium Class C) fly ashes. The specimens were subjected to a 5 percent sodium sulfate solution after two days of moist curing.

Mortar specimens were prepared in a manner similar to that described in ASTM C 1012-90 [2]. All three types of portland cement and all five sources of fly ash were used to prepare mortar specimens for this phase of the study. Four different replacements of fly ash for cement (7.5, 15, 22.5 and 30 percent by weight) were studied in this project. The mortar specimens were exposed to a 5 percent sodium sulfate solution or a synthetic deicer solution (9.5 percent NaCl, 0.25 percent Na_2SO_4) after they reached a compressive strength greater than 2850 psi. A curing study was conducted using various mortar formulations to assess the influence of curing time on the 5 percent sulfate soak test.

Concrete specimens were prepared at the Iowa Department of Transportation. The concrete mixes were proportioned in accordance with IDOT C-3 mix specifications. The concrete mixes employed two different cements (Type I and V), four sources of fly ash (three Class C and 1 Class F), and four different coarse aggregates (Jaben, Lamont, Early Chapel and Montour). A single source of fine aggregate (ACME) was used in the various concrete mixes. Test specimens were moist cured for at least 28 days before immersion in a 10 percent sodium sulfate solution or a synthetic deicer solution (9.5 percent NaCl, 0.5 percent Na_2SO_4).

Alkali Durability

Mortar specimens for alkali silica attack were made in accordance with ASTM C 311-90 [2]. A high alkali (0.81 percent equivalent Na_2O) and a low alkali cement (0.33 percent equivalent Na_2O) were used in the study. All five of the fly ashes and three different fine aggregates (Pyrex glass, standard ASTM C 109 and a Class 5 aggregate) were used to construct test specimens. This study utilized fly ash replacements of 7.5, 15, 22.5, 30 and 50 percent (by weight).

CURRENT STATUS

Chemical Tests

The majority of the chemical tests performed in this study were completed during Phase I of this project. However, there are still x-ray diffraction, thermal analysis, and scanning electron microscopy studies being performed on mortar and paste specimens that have reached failure. Concrete specimens will also be evaluated but presently none of the test specimens have reached failure. Also, a new test method has been found that should increase the accuracy of the tricalcium aluminate determinations in the three portland cements used in this study. Further research is needed to see if the method will also be able to refine the tricalcium aluminate values for the five fly ashes.

Physical Tests

The concentration study is the only mortar bar test that remains to be completed in the sulfate durability phase of the experiment. Recent acquisition of some Lyons rock salt will allow us to include a "real" case into the concentration study.

A total of 104 concrete mixes have been completed by IDOT personnel. Another 52 mixes are currently being planned. At present it appears that the final 52 concrete mixes should be finished by late 1992.

All of the C 311 alkali test specimens have been molded and are currently being stored at 38°C. All of the test specimens will reach one year of age by early summer, 1992.

RESULTS AND DISCUSSION

Abbreviation Summary

The following abbreviations are used throughout the various figures and tables:

DUN = Dundee cement = Northwestern = Type I

DAV = Davenport cement = Type I-II

SDV = South Dakota cement = Type V

CLI = Clinton fly ash (Type F)

LOU = Louisa fly ash (Type C)

OTT = Ottumwa fly ash (Type C)

NE4 = Neal 4 fly ash (Type C)

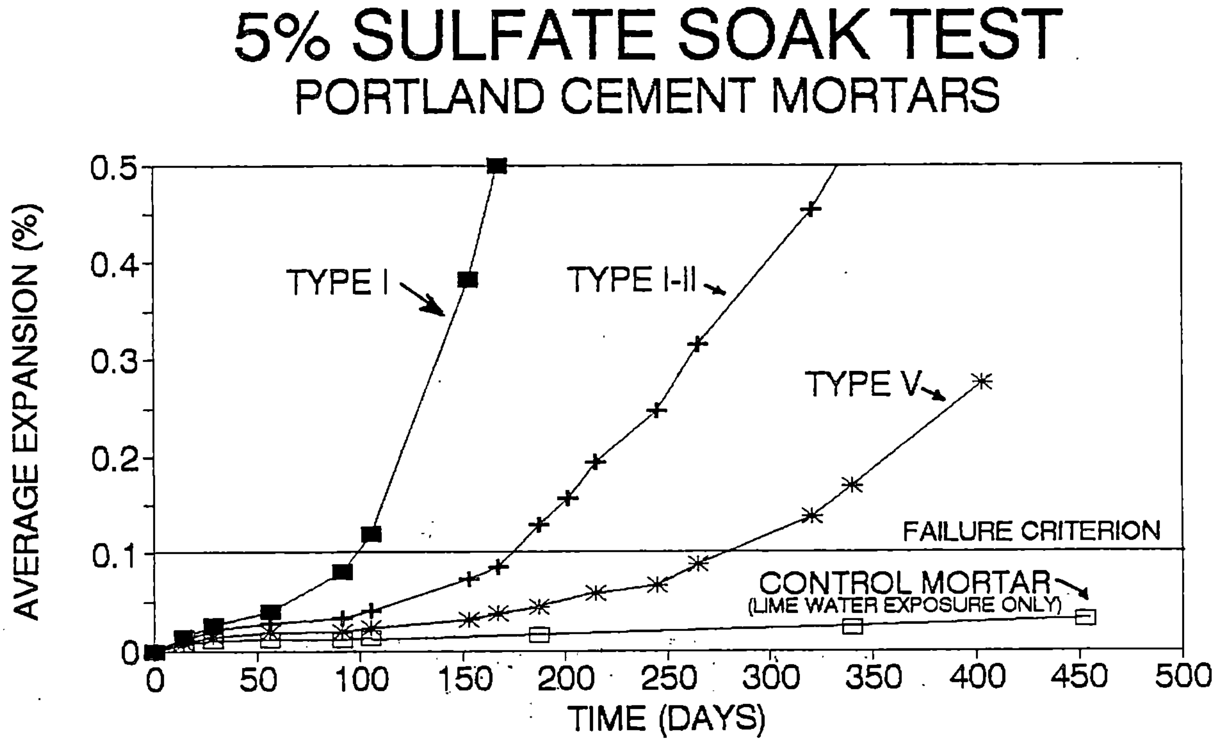
CBF = Council Bluffs fly ash (Type C)

CON = Control Mortar = Cont = Contro

Sulfate Durability Tests

Typical results obtained from the ASTM C 1012 mortar bar tests are shown in Figure 1. Generally the specimens all exhibited delayed expansion; and hence, to reduce the number of graphs needed to portray the information, a criterion of 0.10 percent expansion was defined as "failure." The time required to reach 0.10 percent expansion can then be used to compare the sulfate resistance of mortar bar specimens containing the various cements and fly ashes. A summary of the information is listed in Table 1. Figures 2 through 6 depict this information in a graphical manner. All of the figures were constructed by plotting the relative durability ratio (RDR) versus fly ash replacement. The relative durability ratio (RDR) can be defined as:

$$\text{RDR} = \left(\frac{\text{time required for test specimen to reach 0.10\% growth}}{\text{time required for the Type I-II control specimen to reach 0.10\% growth}}\right) \times 100$$



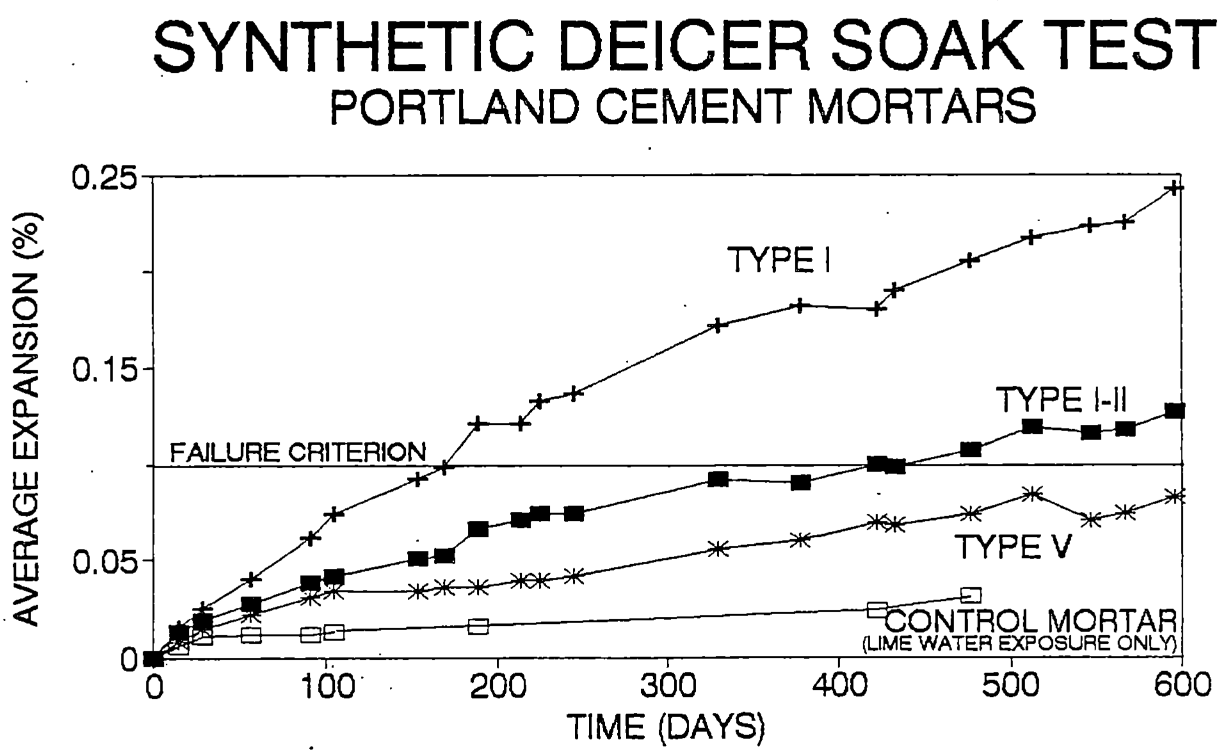


Figure 1. Percent expansion versus time for the three cements used in this study.

Table 1. Time Required for Mortar Bar Specimens to Reach 0.10 Percent Expansion

Treatment = 5 percent Na_2SO_4 soak (as per ASTM C 1012)				
			Cement Type	
Fly Ash	**% Replacement**	**Type I**	**Type I-II**	**Type V**
None	0	98	174	279
Clinton	7.5	92	321	469
	15	153	553	>660*
	22.5	151	>660*	>600*
	30	549	>600*	>660*
Louisa	7.5	123	144	250
	15	147	213	357
	22.5	165	265	468
	30	293	292	499
Ottumwa	7.5	99	124	246
	15	114	141	236
	22.5	93	196	221
	30	128	188	413
Neal 4	7.5	95	132	244
	15	90	144	271
	22.5	108	194	430
	30	101	142	373
Council Bluffs	7.5	81	132	213
	15	65	116	163
	22.5	62	119	189
	30	61	100	216

* = test still in progress

Table 1. Time Required for Mortar Bar Specimens to Reach 0.10 Percent Expansion (continued)

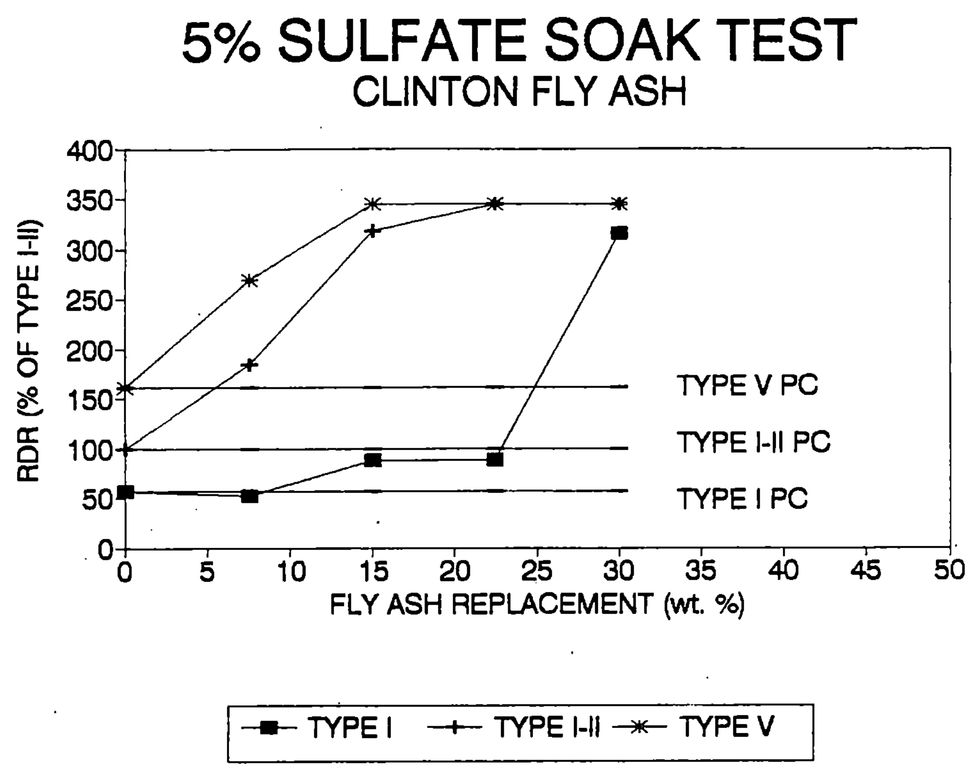
Treatment = synthetic deicer soak (9.5 percent NaCl, 0.25 percent Na_2SO_4)				
			Cement Type	
Fly Ash	**% Replacement**	**Type I**	**Type I-II**	**Type V**
None	0	170	423	>660*
Clinton	7.5	250	567	>660*
	15	461	476	>660*
	22.5	570	>660*	>660*
	30	>660*	>660*	>660*
Louisa	7.5	208	456	>660*
	15	294	478	>660*
	22.5	453	539	>660*
	30	555	519	>660*
Ottumwa	7.5	165	293	584
	15	230	315	>660*
	22.5	342	474	>660*
	30	458	437	>660*
Neal 4	7.5	188	292	>660*
	15	303	468	511
	22.5	425	573	>660*
	30	452	458	>660*
Council Bluffs	7.5	183	300	571
	15	263	370	577
	22.5	301	462	523
	30	422	406	>660*

*** = test still in progress**

The selection of the Type I-II cement control mortar as the divisor of the RDR equation was arbitrary; however, it seems justifiable because it would be economically unrealistic to compare the test mixtures to the Type V control mortar. Note from Table 1, that some of the points plotted on the various figures are only estimates because the specimens had not yet reached the 0.10 percent failure criterion. This was especially true for specimens exposed to the synthetic deicer solution.

Figures 2 through 6 make it easy to evaluate the influence of fly ash replacement on relative durability ratio. The upper portion of each figure depicts the durability of specimens exposed to the 5 percent sodium sulfate soak test, the bottom portion depicts specimens exposed to the synthetic deicer soak test. Note, that the Type I and Type V control specimens that were exposed to the 5 percent sodium sulfate soak solution had RDR values of 56 percent and 160 percent, respectively. The Type I and Type V control specimens that were exposed to the synthetic deicer solution had RDR values of 40 percent and greater than 142 percent, respectively (note that the Type V control mortar has not yet reached 0.10 percent expansion). By definition, the Type I-II cement had a RDR of 100 percent in both instances. The various graphs were constructed by plotting portland cement control points on the y-axis (i.e., at zero percent replacement) and then extending a line from the control point horizontally across the figure. Each control line was then labelled with its respective cement type. The control values are useful when comparing various levels of fly ash replacement in the test mortars. Fly ashes that exhibit trends with a negative slope tended to reduce the relative durability ratio of the mortar specimens with increasing fly ash replacement. Conversely, fly ashes that exhibit trends with a positive slope tended to increase the relative durability ratio of the mortar specimens as the fly ash content was increased.

The various figures (see Figures 2 through 6, top portion of each figure) indicate that Clinton and Louisa fly ashes definitely increased the sulfate resistance of the test mortars placed in the 5 percent sodium sulfate solution. The Ottumwa and Neal 4 fly ashes produced mixed effects (i.e., some positive and some negative), but overall they appear to have little influence on



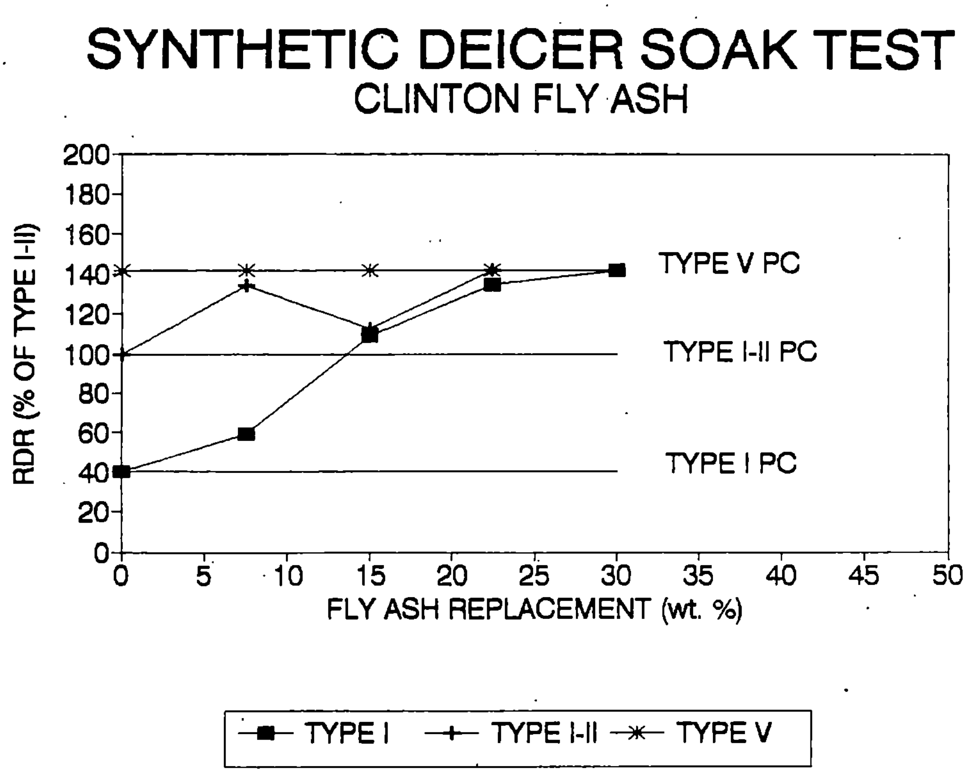
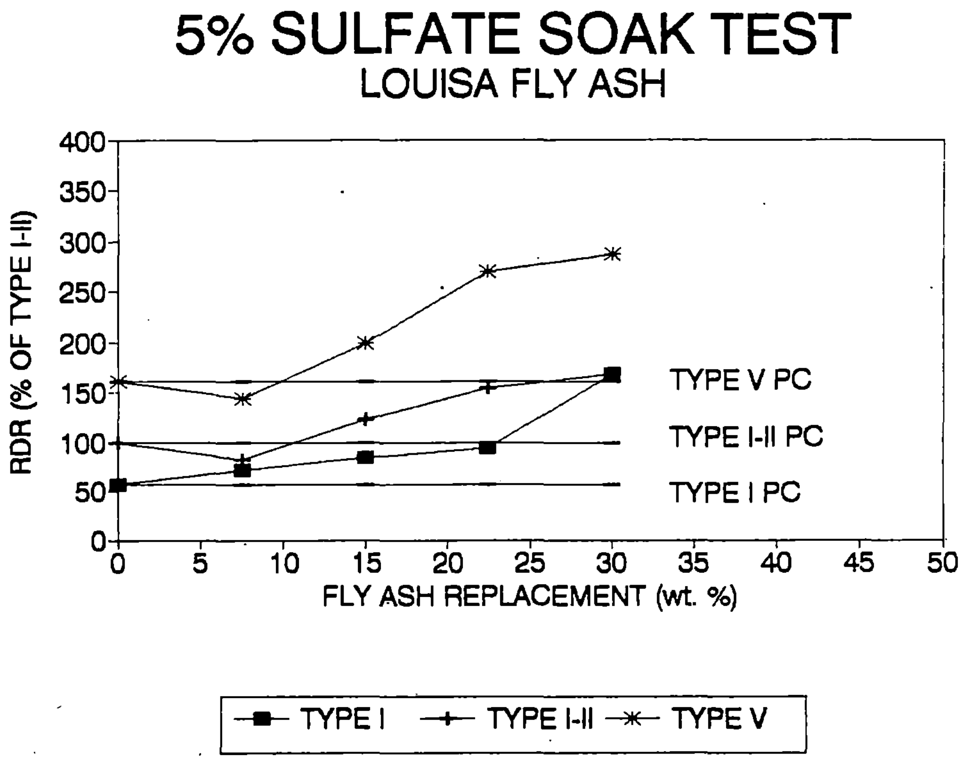


Figure 2. Relative durability ratio versus fly ash replacement for Clinton ash.



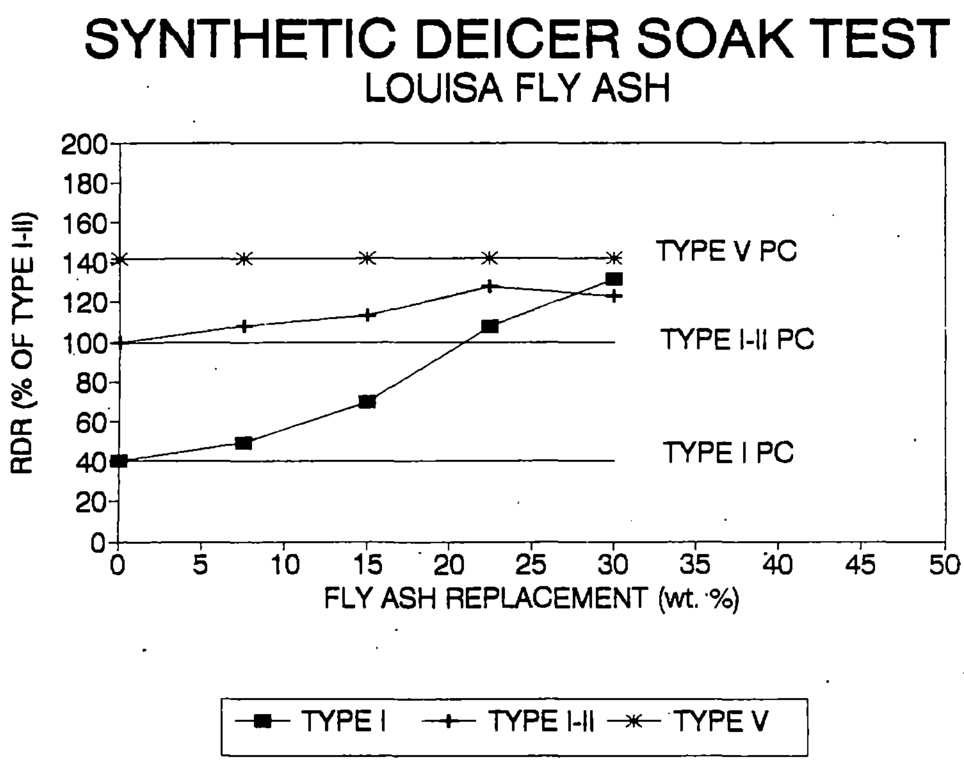
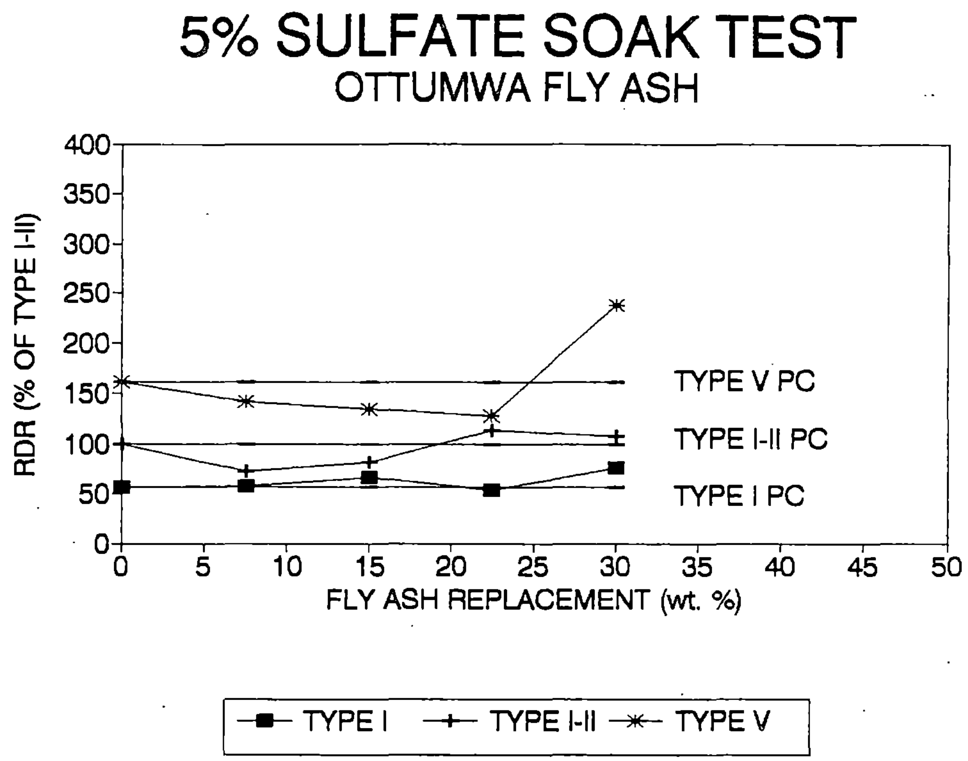


Figure 3. Relative durability ratio versus fly ash replacement for Louisa ash.



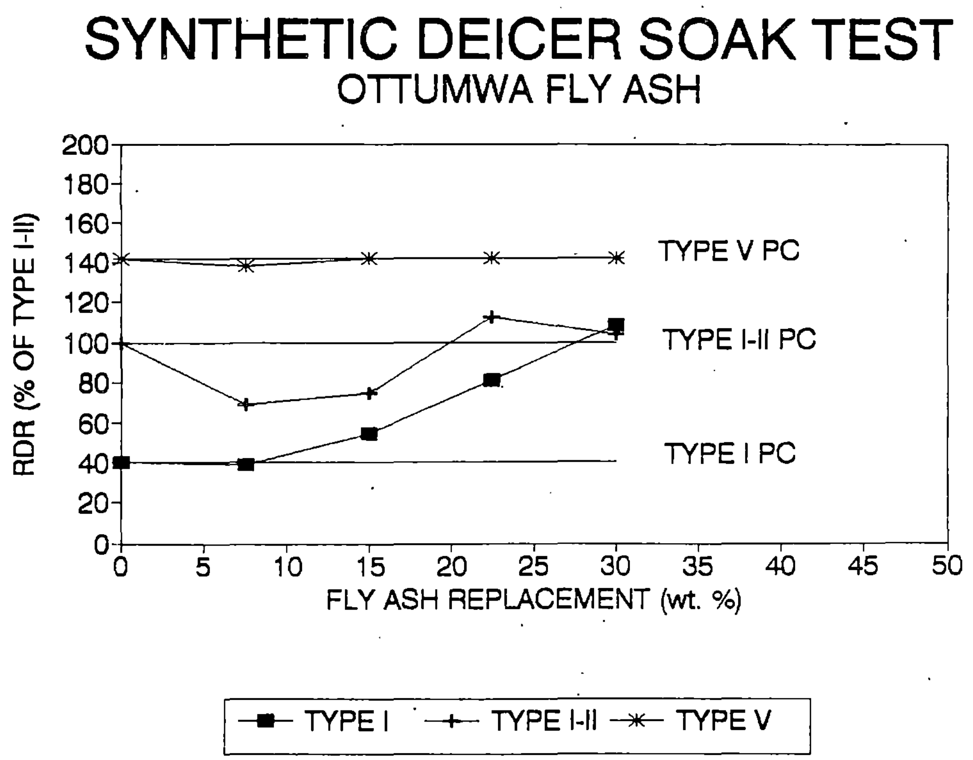
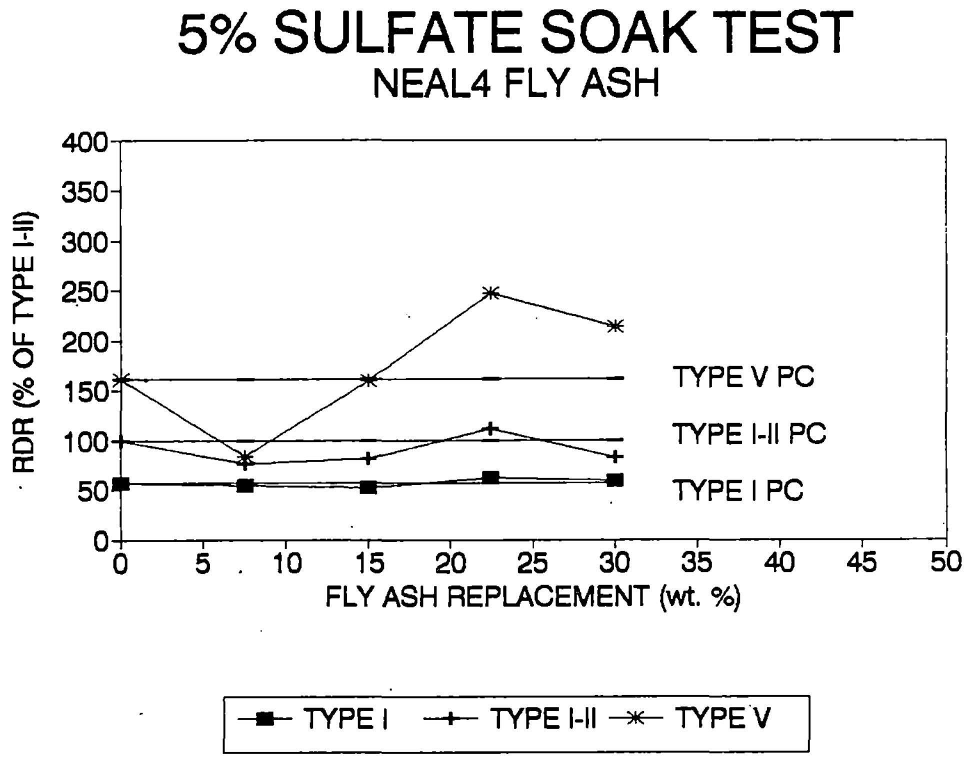


Figure 4. Relative durability ratio versus fly ash replacement for Ottumwa ash.



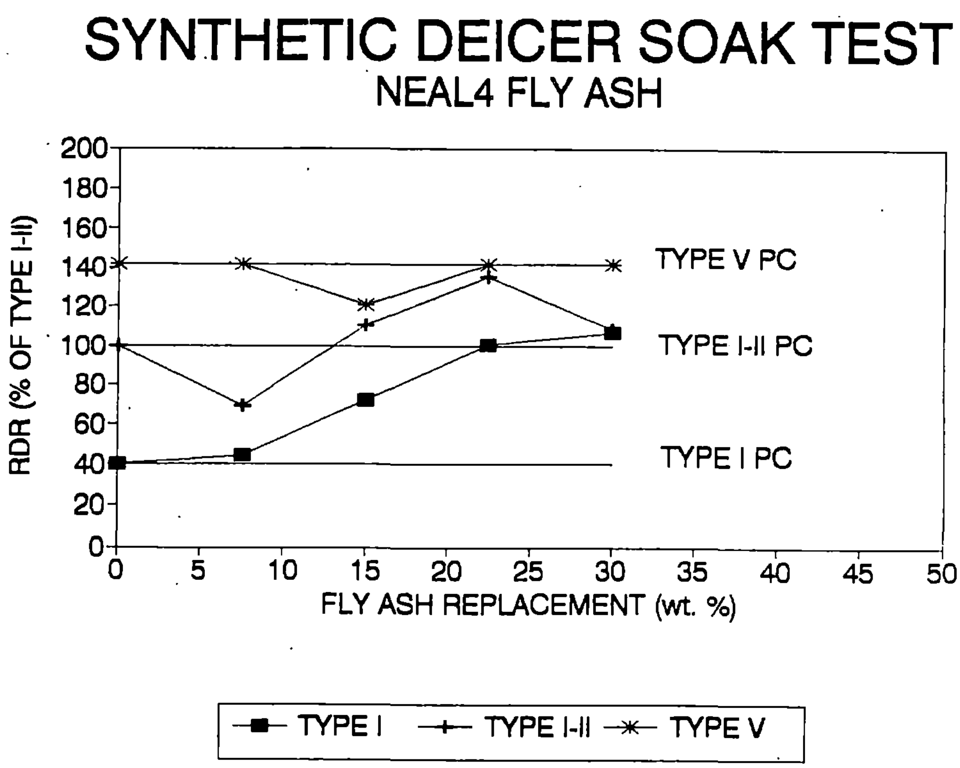
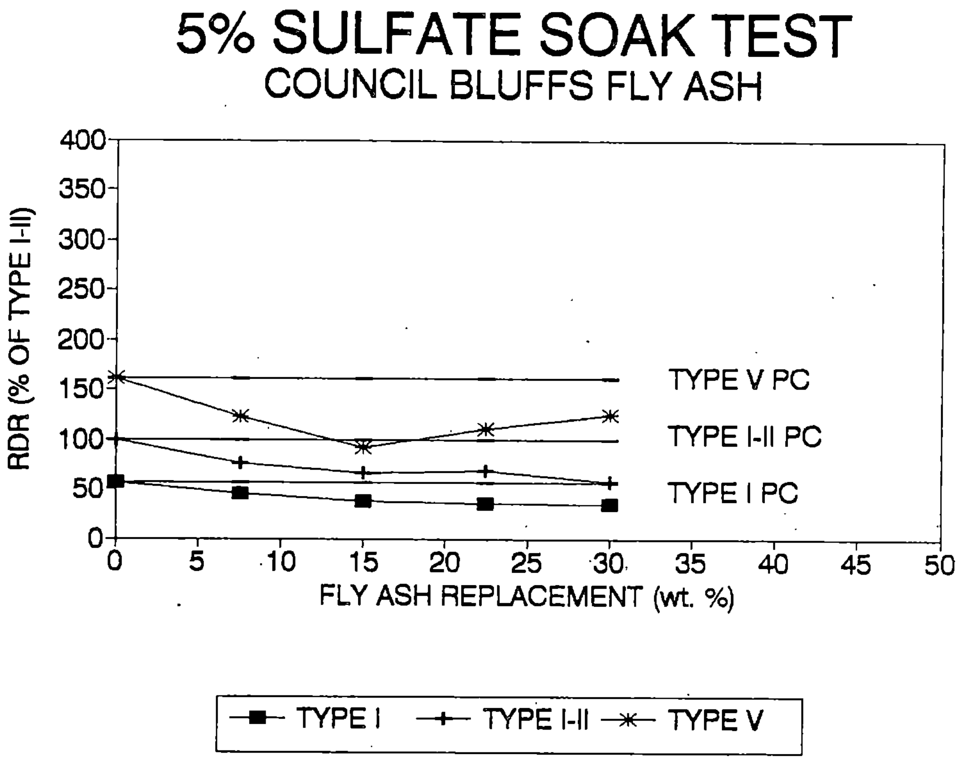


Figure 5. Relative durability ratio versus fly ash replacement for Neal 4 ash.



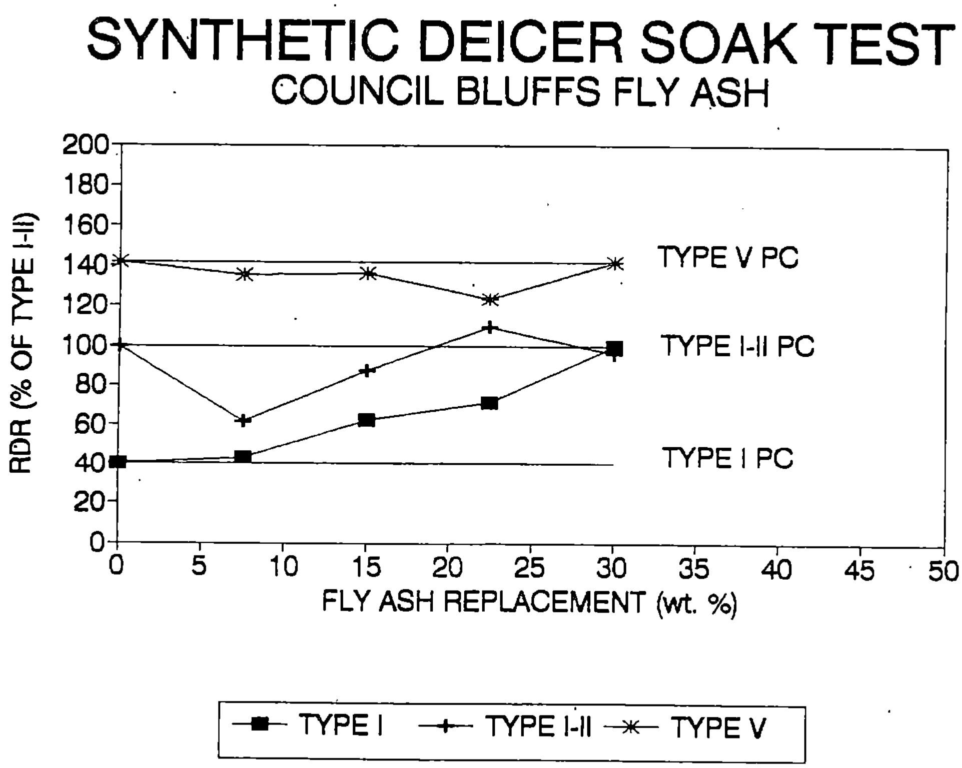


Figure 6. Relative durability ratio versus fly ash replacement for Council Bluffs ash.

the relative durability ratio. The Council Bluffs fly ash was the only fly ash that consistently reduced the relative durability ratio of mortar bar specimens exposed to the 5 percent sodium sulfate solution. The RDR reduction also appeared to be independent of the type of cement used in the mortar.

Test specimens that were submerged in the synthetic deicer solution exhibited trends that were different from those observed with the 5 percent sodium sulfate soak test. In general, the specimens submerged in the synthetic deicer solution took considerably longer to reach failure (0.10 percent expansion) and they also appeared to improve the durability of most of the test specimens (compare the top and bottom halves of Figures 2 through 6). This behavior was most evident in the mortar specimens prepared using Type I portland cement. The Council Bluffs fly ash again performed the worst among the five fly ashes used in this study.

Typically the test specimens were allowed to remain in the 5 percent sodium sulfate solution until their length had increased by more than 0.5 percent; however, there are two exceptions to this statement. First, some of the specimens, especially the specimens containing Council Bluffs fly ash, tended to expand so rapidly that they became very brittle and sensitive to handling. Often these specimens broke after only 0.2 to 0.4 percent expansion. And secondly, the portland cement control mortar specimens were left in the 5 percent sodium sulfate solution until they began to exhibit cracking, this usually occurred after a growth of about 1 to 1.5 percent. All of the test specimens that were initially placed in the synthetic deicer solution are still immersed there because none of them have reached 0.5 percent expansion. These clarifications of testing procedure are important because the chemical testing that is being conducted on the various specimens pertains only to specimens that have been permanently removed from the sulfate tanks. Hence, the samples subjected to chemical testing may be of drastically different ages but are roughly in the same state of physical degradation.

X-ray diffractograms of specific samples are shown in Figures 7 through 10. Samples were prepared for X-ray diffraction (XRD) analysis by: (1) fracturing a section off of a mortar bar; (2) pulverizing the sample for 30 seconds in a shatterbox; (3) sieving the pulverized

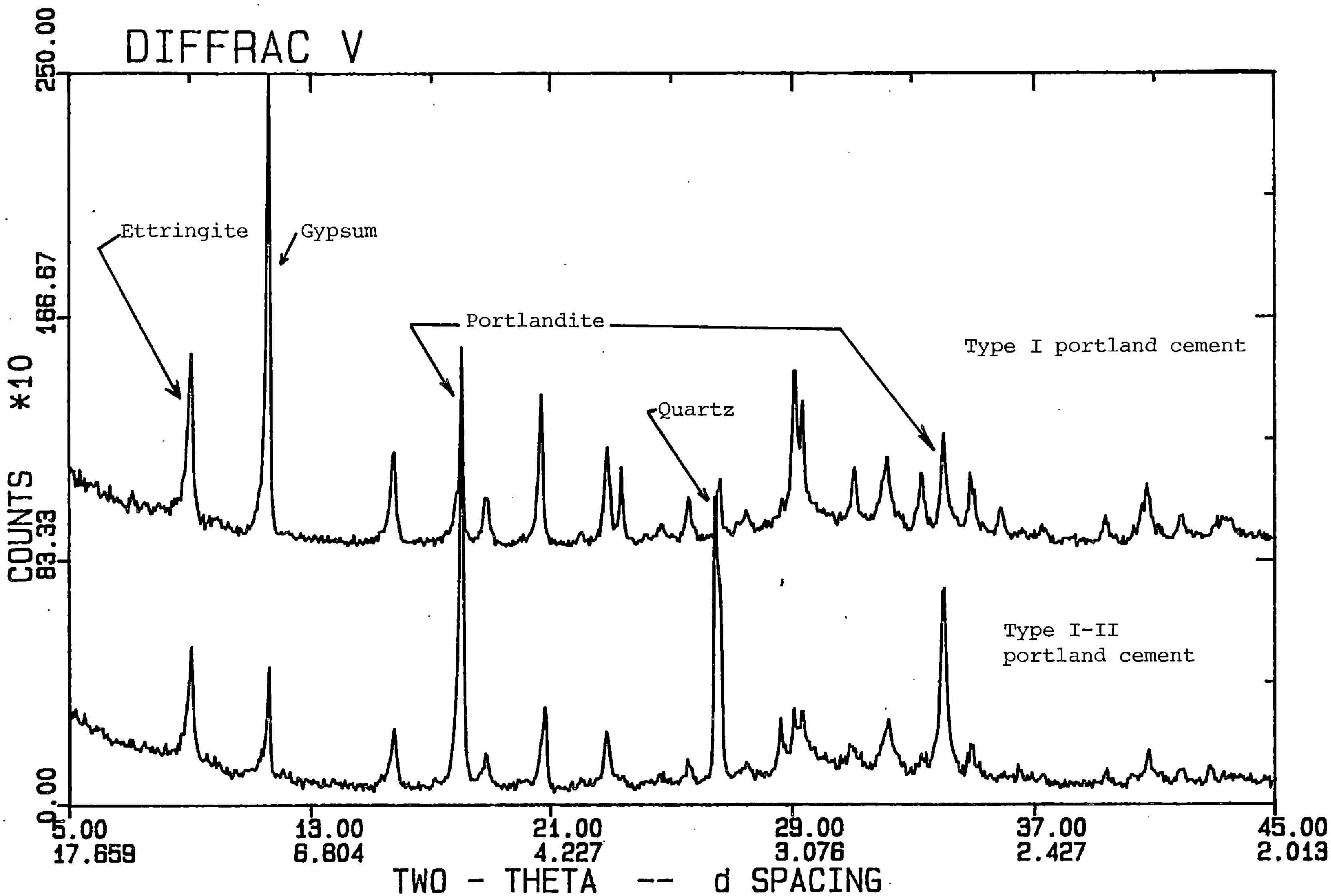


Figure 7. X-ray diffractogram of failed control mortars.

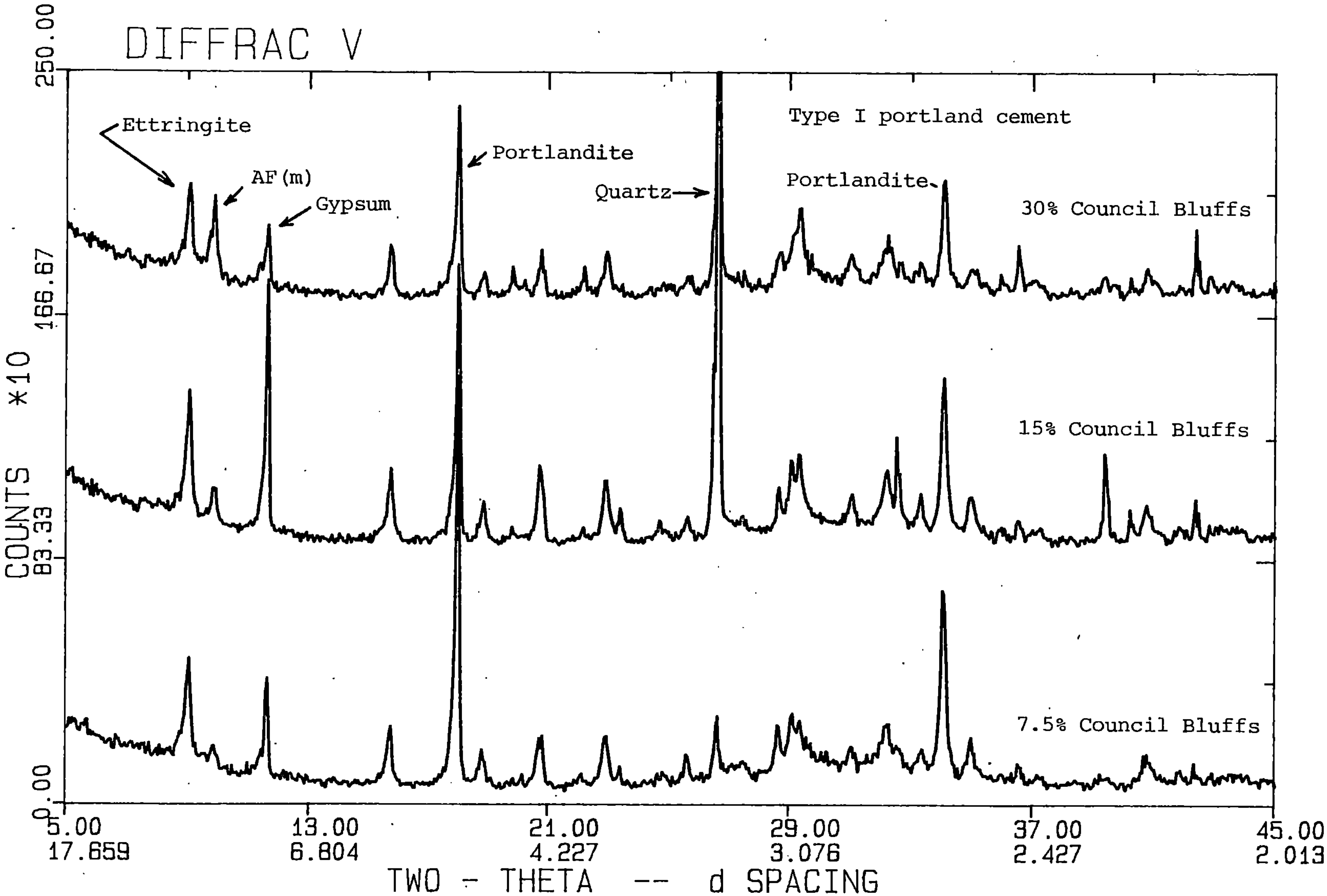


Figure 8. X-ray diffractogram of failed CBF - Type I portland cement mortars.

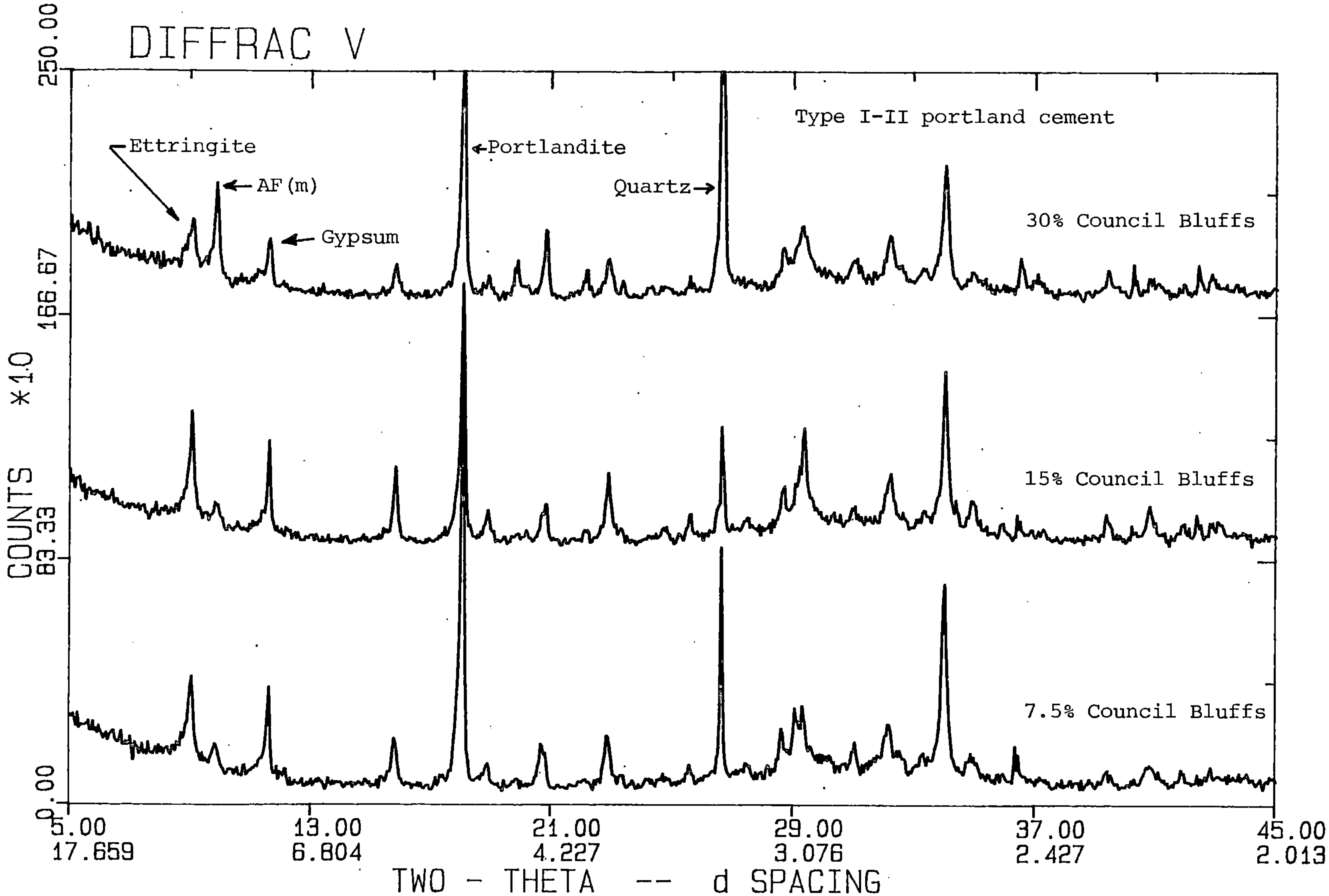


Figure 9. X-ray diffractogram of failed CBF - Type I-II portland cement mortars.

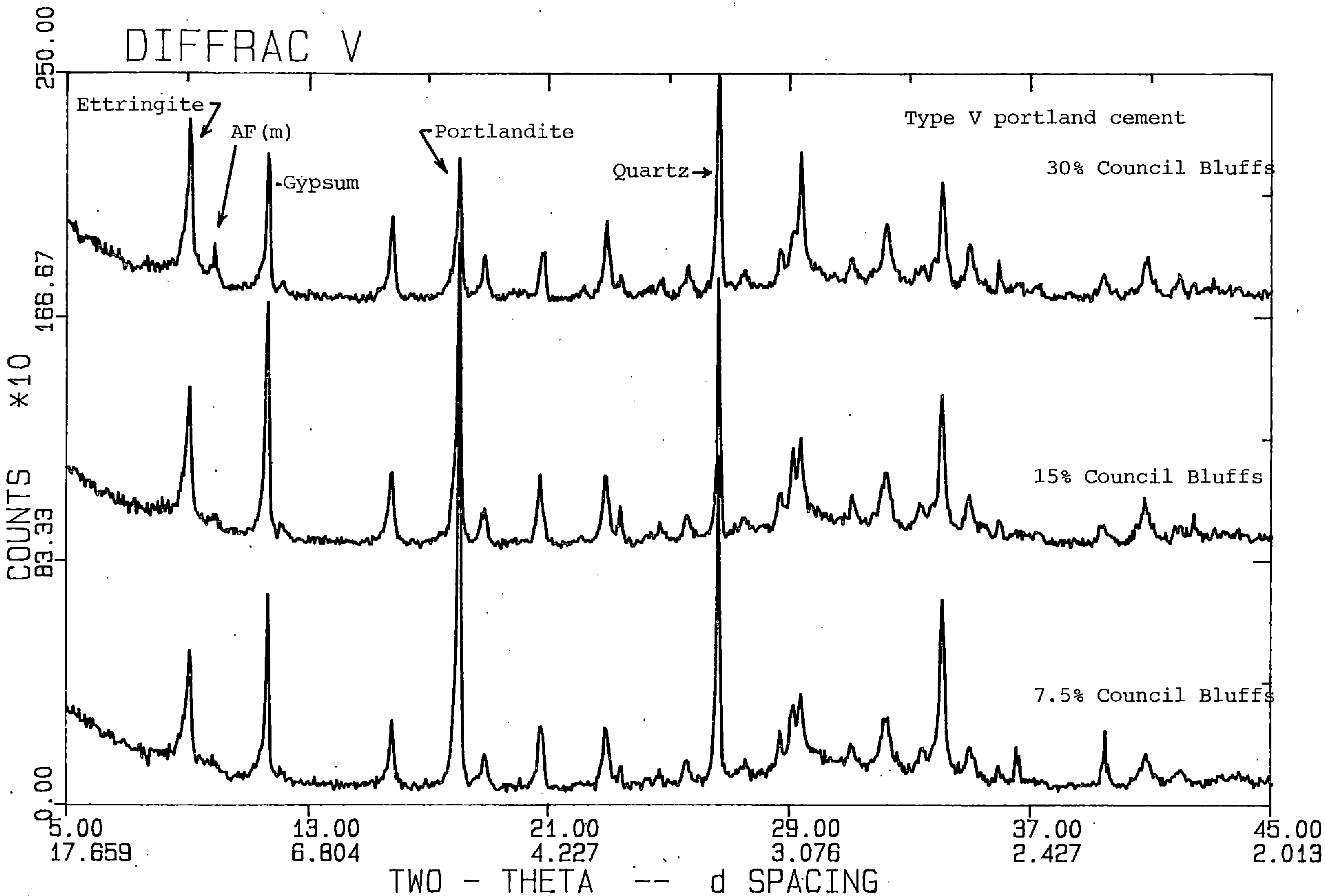


Figure 10. X-ray diffractogram of failed CBF - Type V portland cement mortars.

material through a #100 mesh sieve to remove sand particles; and (4) grinding the material passing the #100 sieve to a fine powder using agate mortar and pestle. X-ray specimens were side-loaded to help avoid preferred orientation. Equipment details have been described in an earlier report [1]. XRD analysis of the portland cement control mortar specimens indicated severe sulfate attack (see Figure 7). The major crystalline minerals identified in the diffractogram were ettringite, gypsum, portlandite (calcium hydroxide) and some quartz (a contaminant from the grinding process). The relative amounts of these compounds varied considerably between the two samples. The Type I sample appeared to contain considerably more gypsum and, therefore, less portlandite than the Type I-II portland cement sample. Obviously, the difference in hardness between a mildly deteriorated mortar and a severely deteriorated mortar may affect the sample pulverization process. Hence, one must view the XRD results qualitatively until a detailed study can be conducted to assess the precision and bias present in the sample pulverization and separation process.

XRD analysis of the fly ash-portland cement mortars yielded results similar to those observed for the portland cement control specimens. The major minerals typically identified in the diffractograms were ettringite, gypsum, portlandite and quartz. However, many of the deteriorated mortar specimens also contained significant amounts of a 8.9 angstrom (Å) mineral that was identified as monosulfoaluminate. Diffractograms for the fly ash exhibiting the poorest sulfate resistance observed in this study are shown in Figures 8 through 10. Each figure depicts the test results obtained from a single type of cement and various replacement levels of the Council Bluffs fly ash. The monosulfoaluminate content of the various mortar specimens appeared to increase with increasing replacement of fly ash for cement.

Thermogravimetric analysis (TG) was performed on the samples that had been studied by XRD analysis. A TA Instruments 2000 thermal analysis system was used throughout this study. The system employs a Hi-Res TGA 2950 thermogravimetric analyzer module. A typical experiment used the following analytical parameters: (1) a scanning rate of 20° per minute, resolution = 5; (2) sample mass of 10 ± 1 milligrams; (3) nitrogen atmosphere, purged at 100 ml/minute; (4) samples were heated from ambient (about 25°C) to about 950°C.

Figure 11 illustrates the results obtained from a mortar specimen containing only Type I portland cement. The mortar specimen had been exposed to the 5 percent sodium sulfate soak test. The thermogram clearly indicates four distinct weight loss events (see the curve labelled TG in Figure 11). These events can be accentuated by taking derivative (with respect to temperature) of the raw data and then plotting the transformed data versus temperature. The transformed curve is referred to as the DTG (derivative of TG) curve and it will be used for discussion purposes throughout the rest of this report. All of the test specimens that will be discussed have been subjected to the 5 percent sodium sulfate soak test (i.e., ASTM C 1012).

Figure 12 depicts DTG versus temperature plots for the Type I and Type I-II portland cement mortar specimens. The various weight loss events, which are now represented as peaks on the DTG versus temperature plots, indicate the decomposition of specific minerals. The first mineral that decomposed was ettringite (decomposition temperature of about 55°C), followed by gypsum (decomposition temperature about 100°C), and portlandite (decomposition temperature about 415°C). The final decomposition event, which occurred at 635°C, was attributed to the removal of hydroxyl anions from the ettringite crystal lattice.

Figures 13 through 15 illustrate the test results that were obtained when using mortars containing the three different portland cements and the Council Bluffs fly ash (i.e., the worst sulfate durability performance that was observed so far in this study). The various figures are all quite similar to the portland cement control specimens; however, one additional thermal event is indicated in the figures. This decomposition event, which occurs at about 132°C, appears to increase with increasing fly ash replacement, this is analogous to the behavior of monosulfoaluminate in the XRD study. Hence, the decomposition event has tentatively been attributed to the presence of monosulfoaluminate (an AF(m) phase) in the various mortar specimens.

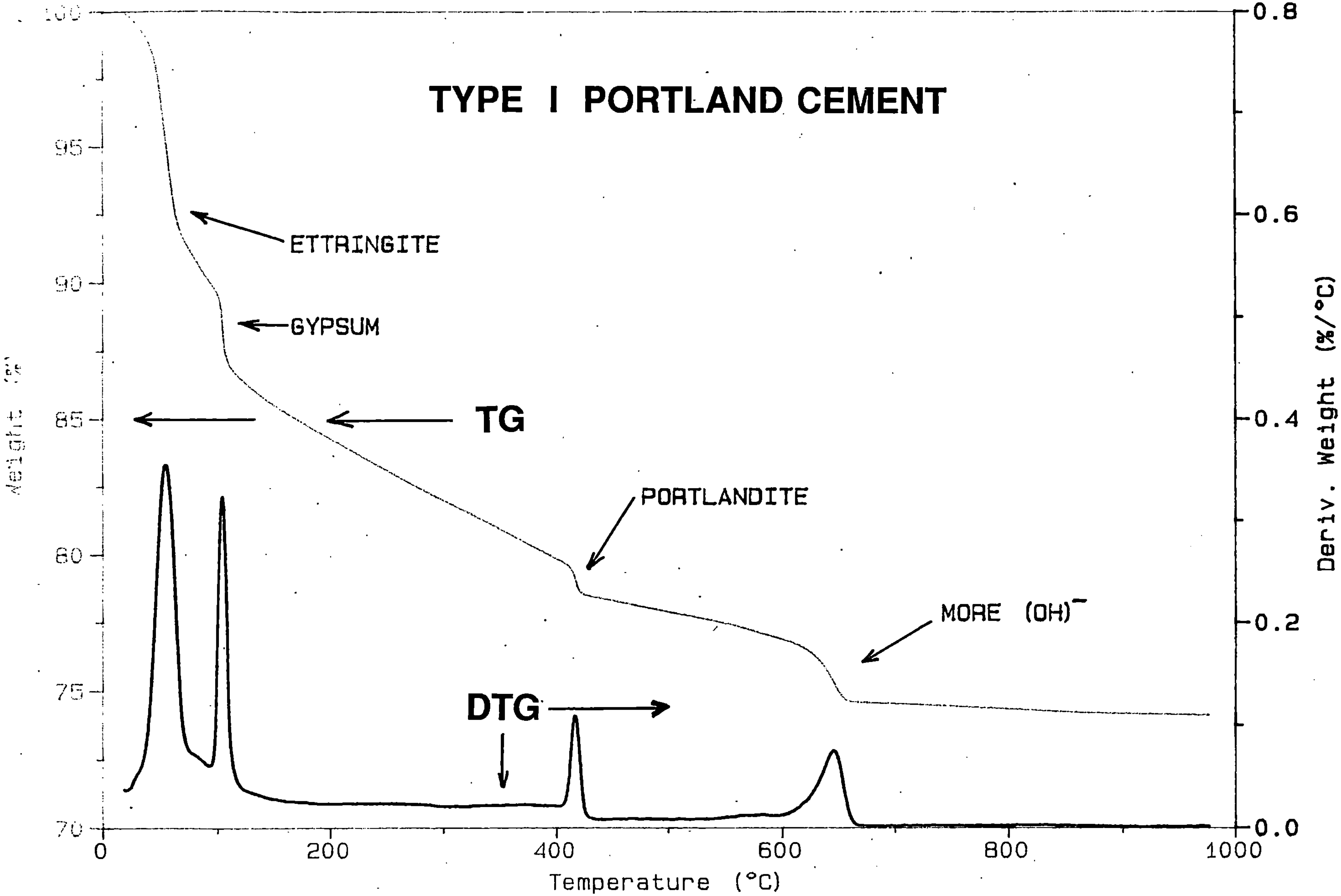


Figure 11. Thermogram for failed Type I portland cement mortar.

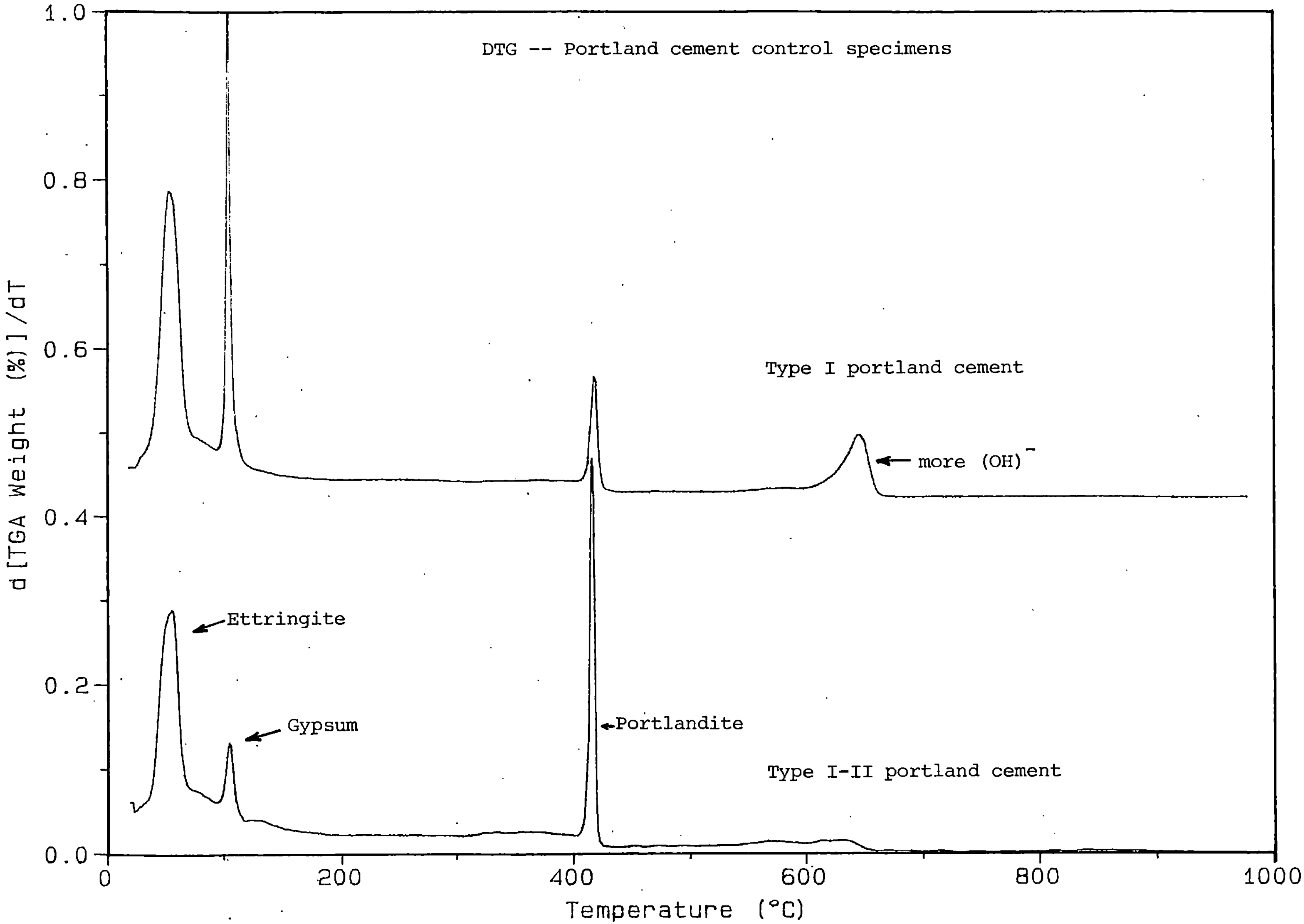


Figure 12. DTG results for failed Type I and I-II portland cement mortars.

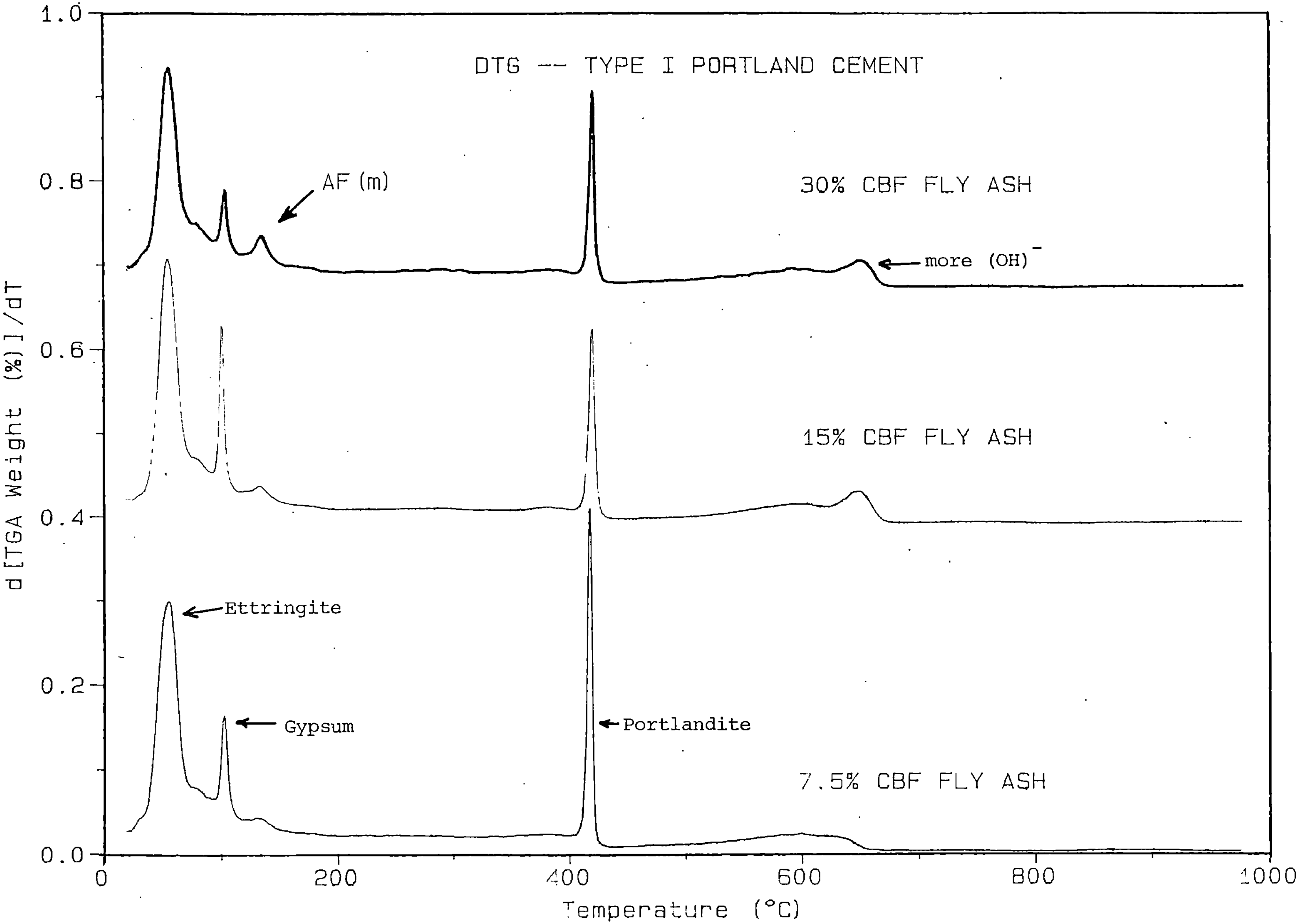


Figure 13. DTG results for failed CBF - Type I portland cement mortars.

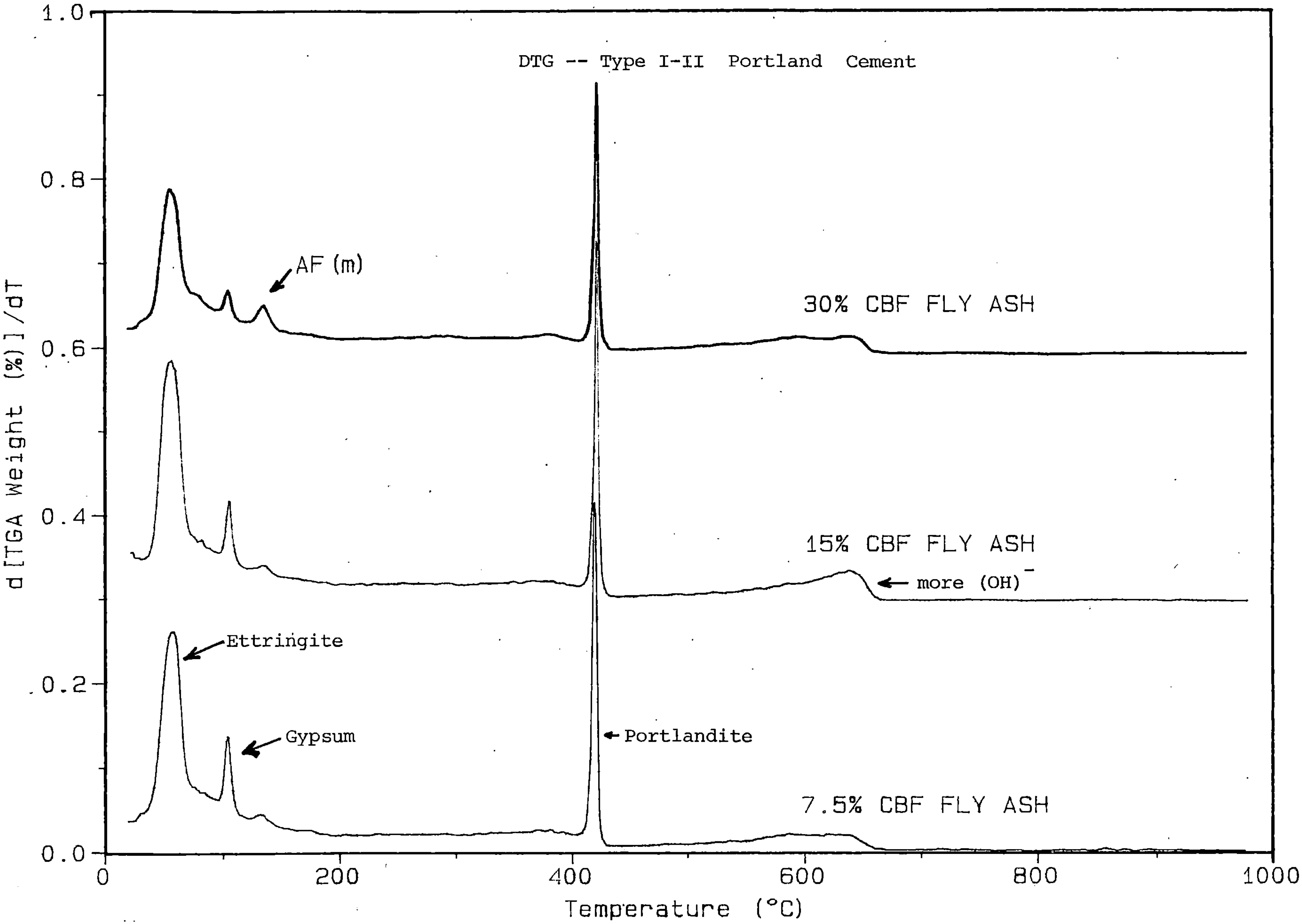


Figure 14. DTG results for failed CBF - Type I-II portland cement mortars.

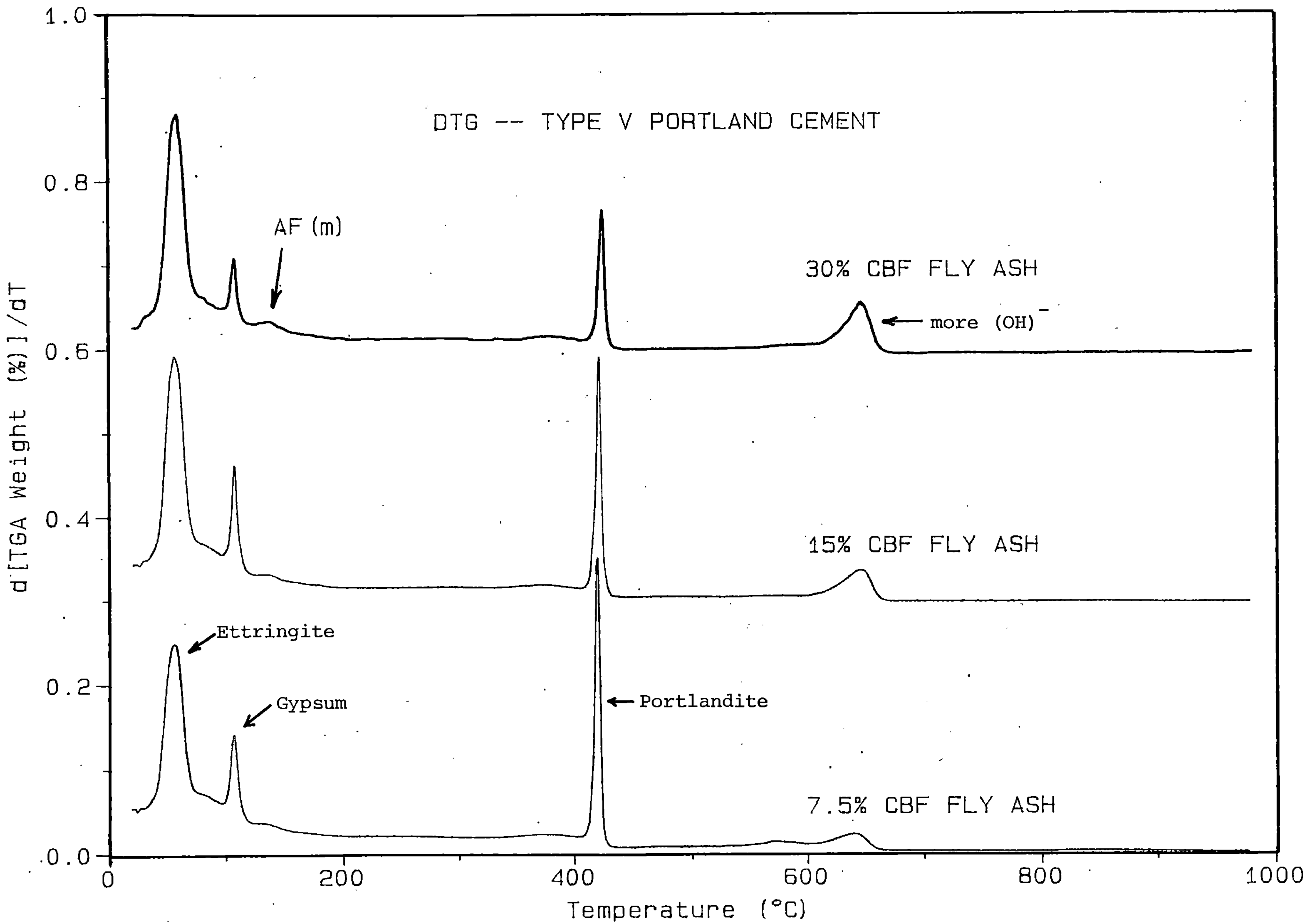


Figure 15. DTG results for failed CBF - Type V portland cement mortars.

Curing Study

The purpose of the curing study was to evaluate the sulfate resistance of mortar specimens that had been subjected to different curing conditions. The following curing conditions were used for this study: (1) 7-day lime water; (2) 28-day lime water and (3) 2-day plastic bag. All of the specimens were cured at room temperature (23 ± 2°C). Only two types of cement (Type I and Type I-II) and two sources of fly ash (Clinton and Council Bluffs) were used in the study. Fly ash replacement was limited to 0, 15 and 30 percent (by weight). Test specimens were placed in the 5 percent sodium sulfate solution after they reached the end of their curing period.

Obviously, the compressive strength of the mortar specimens subjected to the different curing methods varied significantly. ASTM C 109 mortar cubes [2] were used to evaluate the compressive strength of the different mortar mixes, the results of the tests are summarized in Table 2.

Table 2. Compressive strength of C 109 mortar cubes for the various specimens in the curing stage

Cement	Fly Ash	% Replacement	Compressive Strength (psi)		
			2-day plastic	7-day lime	28-day lime
Type I	None	0	2830	4370	5490
Type I	CBF	15	3030	4000	6092
Type I	CBF	30	2730	3660	5550
Type I	CLI	15	2084	3220	4980
Type I	CLI	30	1651	2320	4400
Type I-II	None	0	2950	3870	4940
Type I-II	CBF	15	2850	4272	4832
Type I-II	CBF	30	2260	3120	4400
Type I-II	CLI	15	2680	3540	4840
Type I-II	CLI	30	1980	2610	3730

The results of the curing study are summarized in Table 3. Again, many of the mortar specimens exhibited delayed expansion due to the sulfate exposure. Hence, the time (in days) required to reach failure (0.10 percent in this instance) was used as a measurement of sulfate resistance. At present, about 30 percent of the test specimens are still being monitored. Updated information will be available for the next report.

Table 3. Results of the curing study sulfate durability tests.

Cement	Fly Ash	% Replacement	Days to 0.10 % expansion		
			2-day plastic	7-day lime	28-day lime
Type I	None	0	77	92	103
Type I	CBF	15	83	87	51
Type I	CBF	30	95	77	?a
Type I	CLI	15	159	223	222
Type I	CLI	30	330	>400*	>400*
Type I-II	None	0	204	154	172
Type I-II	CBF	15	146	141	141
Type I-II	CBF	30	156	101	143
Type I-II	CLI	15	>400*	>400*	>400*
Type I-II	CLI	30	>400*	>400*	>400*

*** - test still in progress**
a - specimens broke at 50 and 65 days of exposure, expansions were less than 0.03% in both instances

Paste Study

Portland cement-fly ash paste specimens were prepared using the Type I portland cement and Council Bluffs and Clinton fly ashes. All of the paste mixtures were proportioned using 0, 15, or 30 percent (weight percent) fly ash replacement and a water to cement plus fly ash ratio of 0.35. The pastes were mixed using the procedure developed earlier at this laboratory [3]. After mixing, the paste was immediately poured into autoclave bar molds (1" x 1" x 11.25" dimensions), compacted via a hand tamper, and then struck off level to the top of the molds. The paste bars were moist cured for two days before being immersed in the 5 percent sodium sulfate solution.

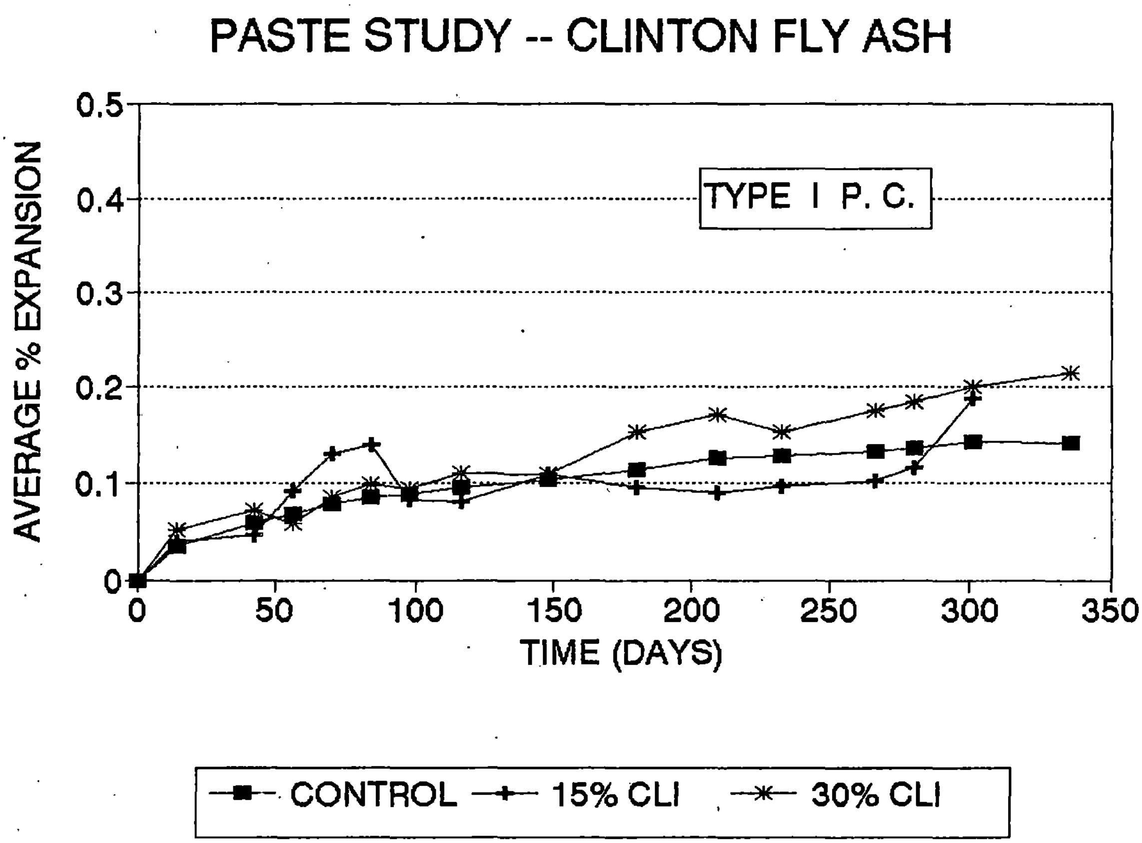
The results of the paste study are illustrated in Figure 16. To date only one of the specimens (a mix containing Clinton fly ash) has exhibited severe delayed expansion due to sulfate exposure. All of the remaining specimens have expanded significantly (about 0.2 percent) but they are only exhibiting a gradual rate of growth. Hence, one may surmise that the 0.10 percent failure criterion (adopted for the mortar specimens) does not apply to the paste specimens. A new series of test specimens are being planned to investigate the influence of water/cement + fly ash ratio on the sulfate resistance of portland cement-fly ash pastes.

Concrete Study

A summary of the details pertaining to the concrete mixes made by Iowa Department of Transportation personnel is listed in Table 4. This table summarizes only the concrete mixes made during 1991. all of the concrete mixes had air contents of 6 ± 1 percent and slumps of 2 ± 0.5 inches. The 28-day compressive strengths of the different mixes varied from a low of about 5000 psi (typically mixes containing Clinton ash) to a high of over 7000 psi. Obviously, none of these new test specimens have yet exhibited any sulfate induced deterioration.

Typical results obtained from the sulfate durability tests conducted on the first 52 concrete mixes (i.e, Phase I specimens), are shown in Figures 17 through 20. Growth and sonic modulus test results from all the concrete specimens have been plotted and placed in Appendix I. This was done only to reduce the number of figures present in the main body of the report. All of the information contained in Appendix I is very important to this research project; however, as will be discussed shortly, the concrete specimens are just beginning to show a response to the sulfate treatment.

The concrete specimens that will be described in this section were all among the first mixed for this project. The various concrete mixes contained Type I portland cement, Jabens coarse aggregate, Acme sand, and fly ash from either Council Bluffs or Clinton. Note, that these



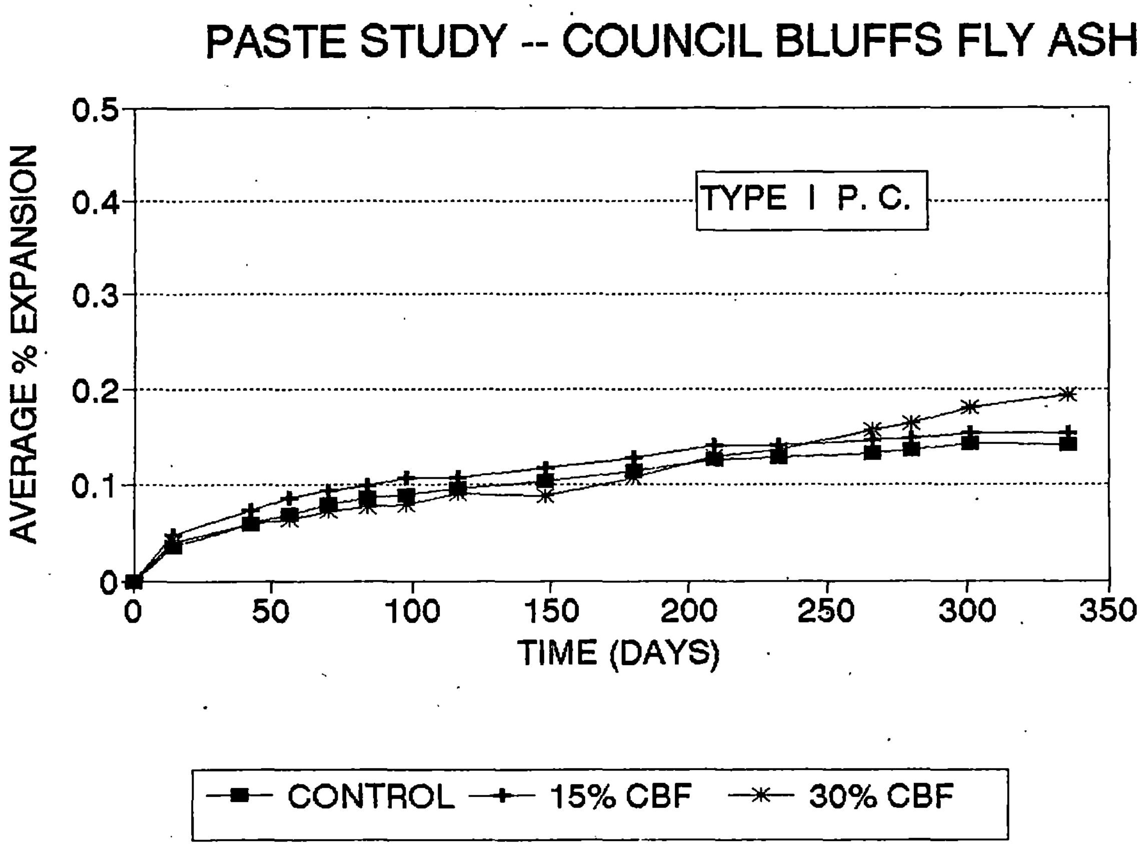


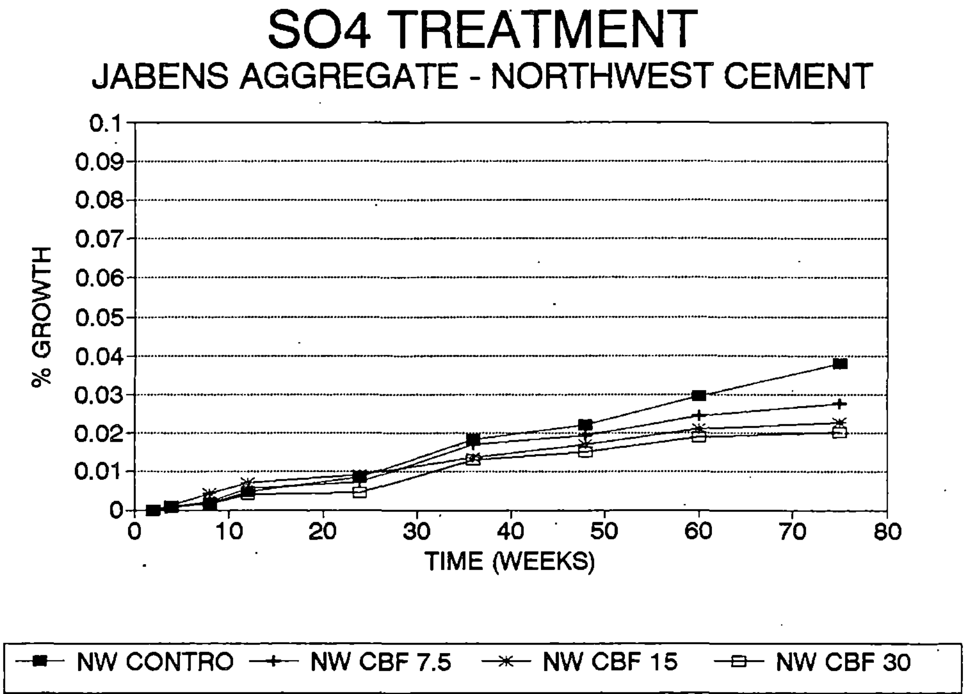
Figure 16. Percent expansion versus time for the paste specimens.

Table 4. Summary of Concrete Mix Parameters

Coarse Aggregate: Montour								
Mix #	**Cement**	**Fly Ash**	**Ash %**	**Water/ Cement**	**Air %**	**Slump (inches)**	**Unit Wt. (pcf)**	**28-day Comp. Str. (psi)**
53	Dundee	Ottumwa	0	0.439	6.6	2.75	142.0	5920
54			7.5	0.405	6.8	1.75	143.2	-
55			15	0.401	5.6	2.00	144.0	6640
56			30	0.371	5.8	2.00	144.0	7080
57	Dundee	C. Bluffs	7.5	0.429	5.4	1.75	144.0	-
58			15	0.394	5.8	1.75	144.0	6320
59			30	0.375	6.0	1.75	144.0	6230
60	Dundee	Clinton	7.5	0.422	5.6	1.75	142.4	-
61			15	0.403	5.6	1.75	144.0	6430
62			30	0.408	5.7	1.75	143.2	6050
63	Dundee	Louisa	7.5	0.422	5.8	2.00	144.4	-
64			15	0.403	5.5	1.75	144.8	7020
65			30	0.380	5.6	2.25	144.4	7120
66	S. Dakota	Ottumwa	0	0.424	5.8	2.25	143.6	6860
67			7.5	0.422	5.8	2.25	144.8	-
68			15	0.415	5.5	2.25	145.6	6850
69			30	0.390	6.1	2.00	144.0	7220
70	S. Dakota	C. Bluffs	7.5	0.428	6.0	2.00	143.2	-
71			15	0.429	6.0	2.00	144.2	6750
72			30	0.403	6.5	2.25	144.0	5930
73	S. Dakota	Clinton	7.5	0.458	6.5	2.50	141.6	-
74			15	0.433	5.8	1.75	143.6	5080
75			30	0.446	5.8	2.00	143.2	5170
76	S. Dakota	Louisa	7.5	0.440	6.0	2.50	143.6	-
77			15	0.448	6.0	2.50	143.6	6800
78			30	0.408	6.0	2.00	144.4	7000

Table 4. Summary of Concrete Mix Parameters (continued)

Mix #	Cement	Fly Ash	Ash %	Water/ Cement	Air %	Slump (inches)	Unit Wt. (pcf)	28-day Comp. Str. (psi)
Coarse Aggregate: Early Chapel								
79	Dundee	Ottumwa	0	0.476	5.7	1.75	142.8	5700
80			7.5	0.464	5.4	1.75	143.6	-
81			15	0.466	5.5	2.00	144.0	5890
82			30	0.446	5.6	2.00	143.2	5680
83	Dundee	C. Bluffs	7.5	0.476	5.7	2.25	143.2	-
84			15	0.457	5.3	1.75	144.0	5460
85			30	0.441	6.2	2.00	142.0	5770
86	Dundee	Clinton	7.5	0.476	5.5	2.00	142.4	-
87			15	0.471	5.7	1.75	142.4	5460
88			30	0.455	5.6	2.00	141.6	4900
89	Dundee	Louisa	7.5	0.476	6.1	2.00	142.4	-
90			15	0.462	5.4	2.00	143.2	5950
91			30	0.431	5.4	1.75	144.4	6360
92	S. Dakota	Ottumwa	0	0.466	5.5	1.75	143.6	6450
93			7.5	0.458	5.6	1.75	142.8	-
94			15	0.448	5.5	2.25	143.6	6030
95			30	0.436	6.1	2.25	143.2	5900
96	S. Dakota	C. Bluffs	7.5	0.458	6.1	1.75	143.2	-
97			15	0.462	5.8	1.75	143.6	5960
98			30	0.436	6.5	2.00	142.8	6180
99	S. Dakota	Clinton	7.5	0.476	5.9	2.25	142.8	-
100			15	0.476	5.5	2.00	143.2	5420
101			30	0.469	5.9	2.25	141.6	4710
102	S. Dakota	Louisa	7.5	0.476	6.1	1.75	142.8	-
103			15	0.453	5.4	1.75	143.6	5750
104			30	0.436	5.5	1.75	143.6	6490



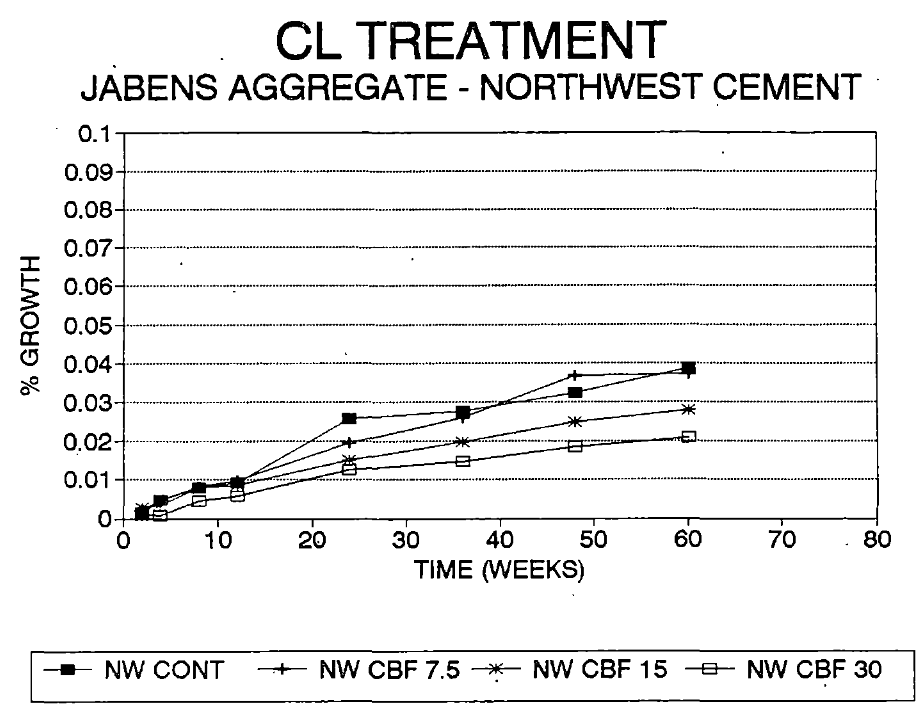
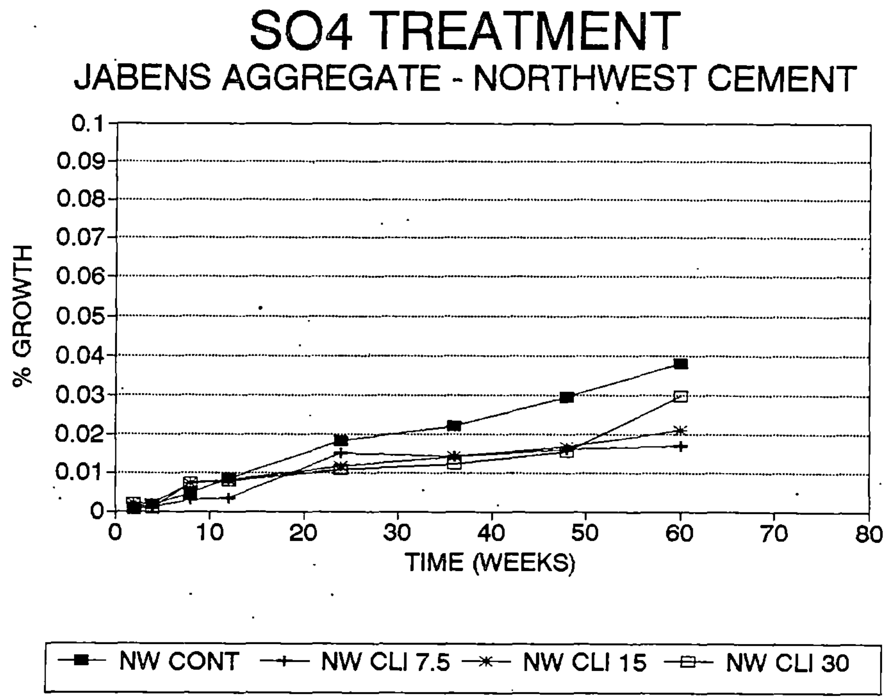


Figure 17. Typical expansion test results for concrete specimens containing Type I portland cement, Council Bluffs fly ash and Jabens coarse aggregate.



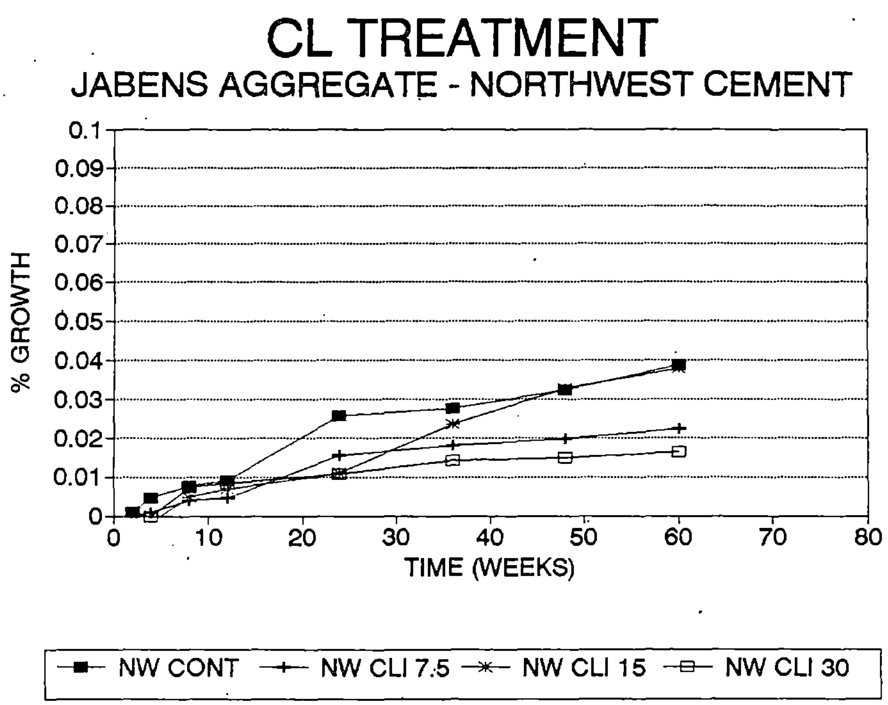
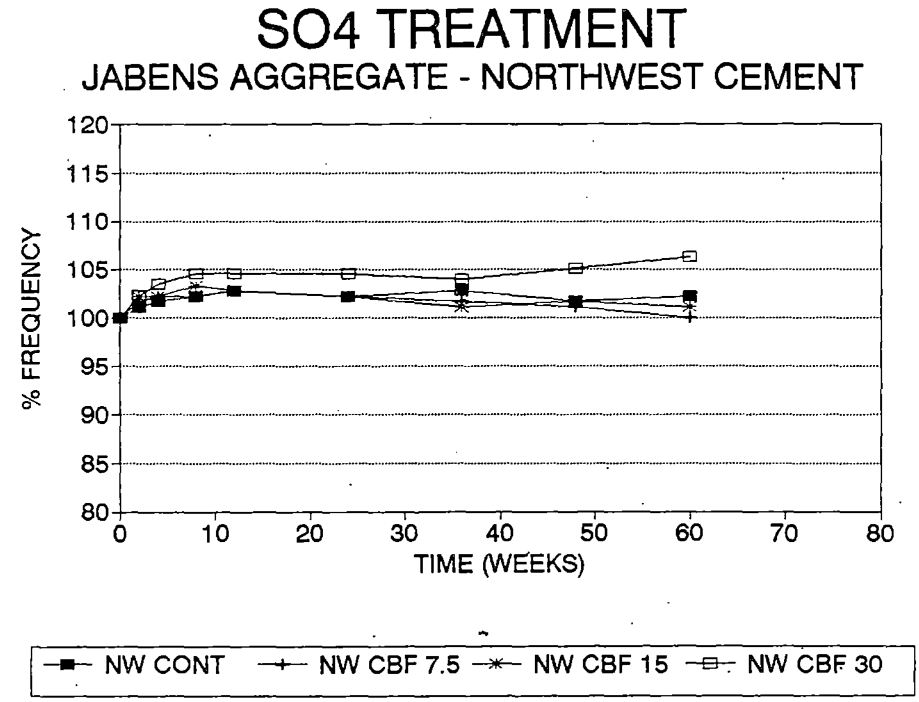


Figure 18. Typical expansion test results for concrete specimens containing Type I portland cement, Clinton fly ash and Jabens coarse aggregate.



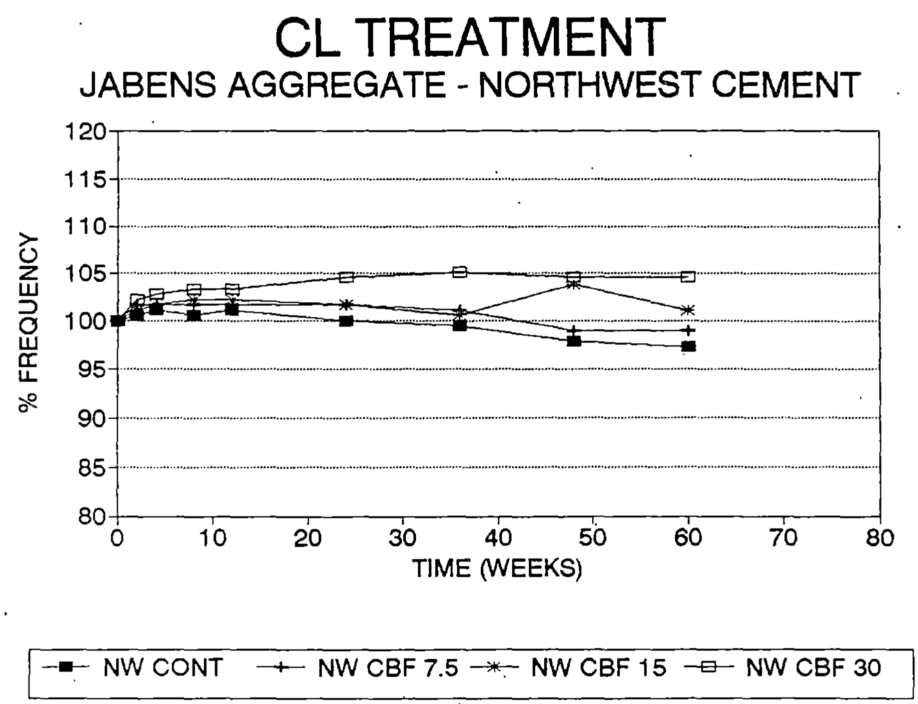
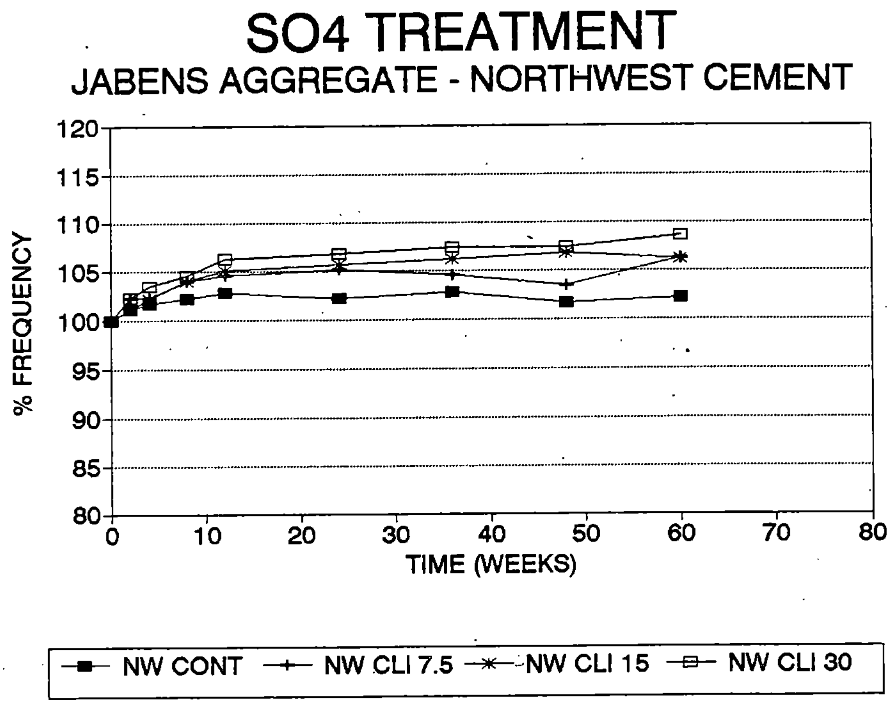


Figure 19. Typical sonic modulus test results for concrete specimens containing Type I portland cement, Council Bluffs fly ash and Jabens coarse aggregate.



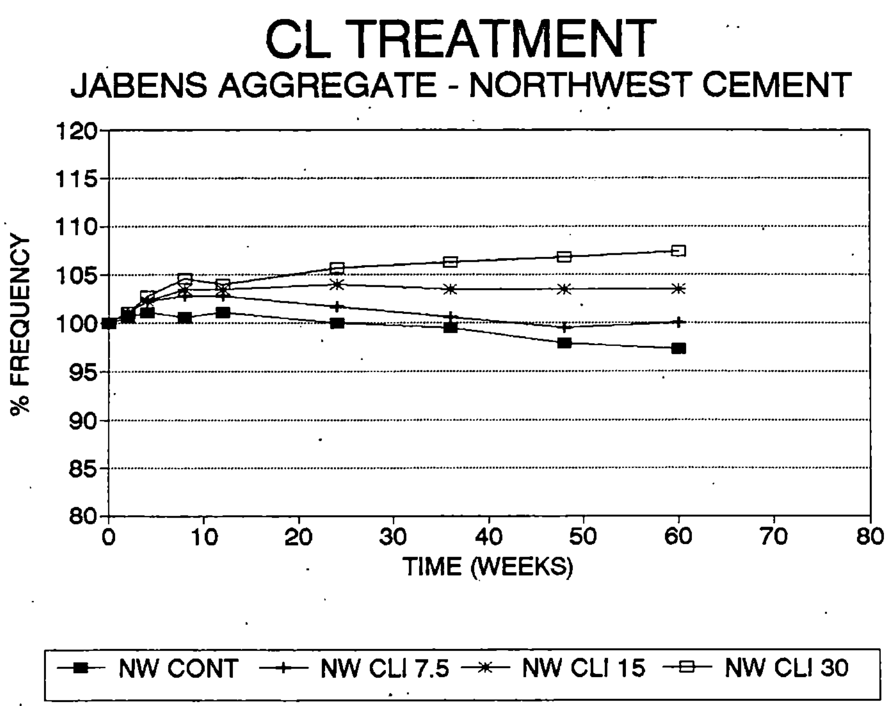


Figure 20. Typical sonic modulus test results for concrete specimens containing Type I portland cement, Clinton fly ash and Jabens coarse aggregate.

two fly ashes performed very differently in the mortar bar study. The Clinton fly ash consistently increased the sulfate resistance of mortar bar specimens while the Council Bluffs fly ash consistently decreased the sulfate resistance of mortar bar specimens. Hence, if the concrete specimens perform similar to the mortar bar specimens these two mixes should exhibit the largest differences.

The results of growth measurements on the two sets of concrete specimens are shown in Figures 17 and 18. Presently the control specimens all have expanded about 0.04 percent, regardless of the sulfate content of the solution that they were immersed in. Specimen growth appears to decrease with increasing fly ash replacement. Also, the Council Bluffs fly ash has yet to exhibit any detrimental influence on the sulfate durability of the concrete specimens.

Results of the sonic modulus measurements (see Figures 19 and 20) are in good agreement with the growth data. In general, the relative dynamic modulus (denoted as percent frequency in the various graphs) appeared to be relatively stable or at the early stages of decline. Dynamic modulus appears to increase with increasing replacement of fly ash for cement.

Visual inspection of the various test specimens was in general agreement with both the growth measurements and the sonic modulus tests. Typically one would notice a decrease in surface spalling with increasing fly ash content. However, the visual inspection also clearly indicated a difference in appearance between the concrete specimens containing Clinton fly ash and all the remaining test specimens. Often the Type I portland cement mixes that contained Clinton fly ash exhibited less surface deterioration than even the Type V control specimens.

Alkali Reactivity Tests

The preliminary results of the alkali reactivity tests are shown in Figures 21 through 35. All of the figures were constructed in a similar manner. The vertical axis portrays the linear expansion of the various fly ash, cement and aggregate mixtures while the horizontal axis denotes the time at which the specimens were measured. Note, that the vertical scale on the various figures may be quite different. This was found to be primarily dependent on the type of aggregate used in the mortar bar specimen. The figures were constructed in this manner to contrast the use of high alkali (0.81 percent equivalent Na_2O) and low alkali (0.33 percent equivalent Na_2O) cement. The failure criteria suggested by the ASTM are 0.02 percent expansion at 14 days, 0.05 percent expansion at 3 months and 0.10 percent expansion at 6 months [4]; the results from the long-term tests always have precedence over the short-term results [4].

Figures 21 through 25 depict a "worst case" scenario because all of the mortar bar specimens were made with an extremely alkali reactive aggregate (crushed Pyrex glass). The mortar bar specimens made with the high-alkali cement expanded rapidly during the first two to three months of the experiment and have remained nearly constant since that time. In contrast, control specimens made with the low-alkali cement have exhibited a rather slow (but steady) increase in length since the beginning of the experiment. The replacement of fly ash for portland cement produced a wide variety of different results that appeared to depend on both the source of fly ash and level of replacement. Most of the fly ashes exhibited a "pessimum" type behavior at some level of fly ash replacement; however, the alkali content of the cement also appeared to influence this behavior. Hence, no simple relationship was observed between the alkali content (either total or available) of the fly ashes and their performance in the C 311 mortar bar study.

Mortar bar specimens containing Clinton fly ash (Class F ash) typically performed the best (i.e., expanded the least), this was observed in test specimens that contained either the high or the low alkali cement. Many of the Class C fly ashes were also quite effective in reducing the expansion of mortar bar specimens containing the high alkali cement, especially at high fly ash replacements. However, the Class C fly ashes also tended to increase the expansion of specimens containing the low alkali cement. Louisa fly ash, at replacements of 7.5 and 15 percent, was the only Class C ash that could keep the expansion of the low alkali mortar specimens under 0.10 percent at six months.

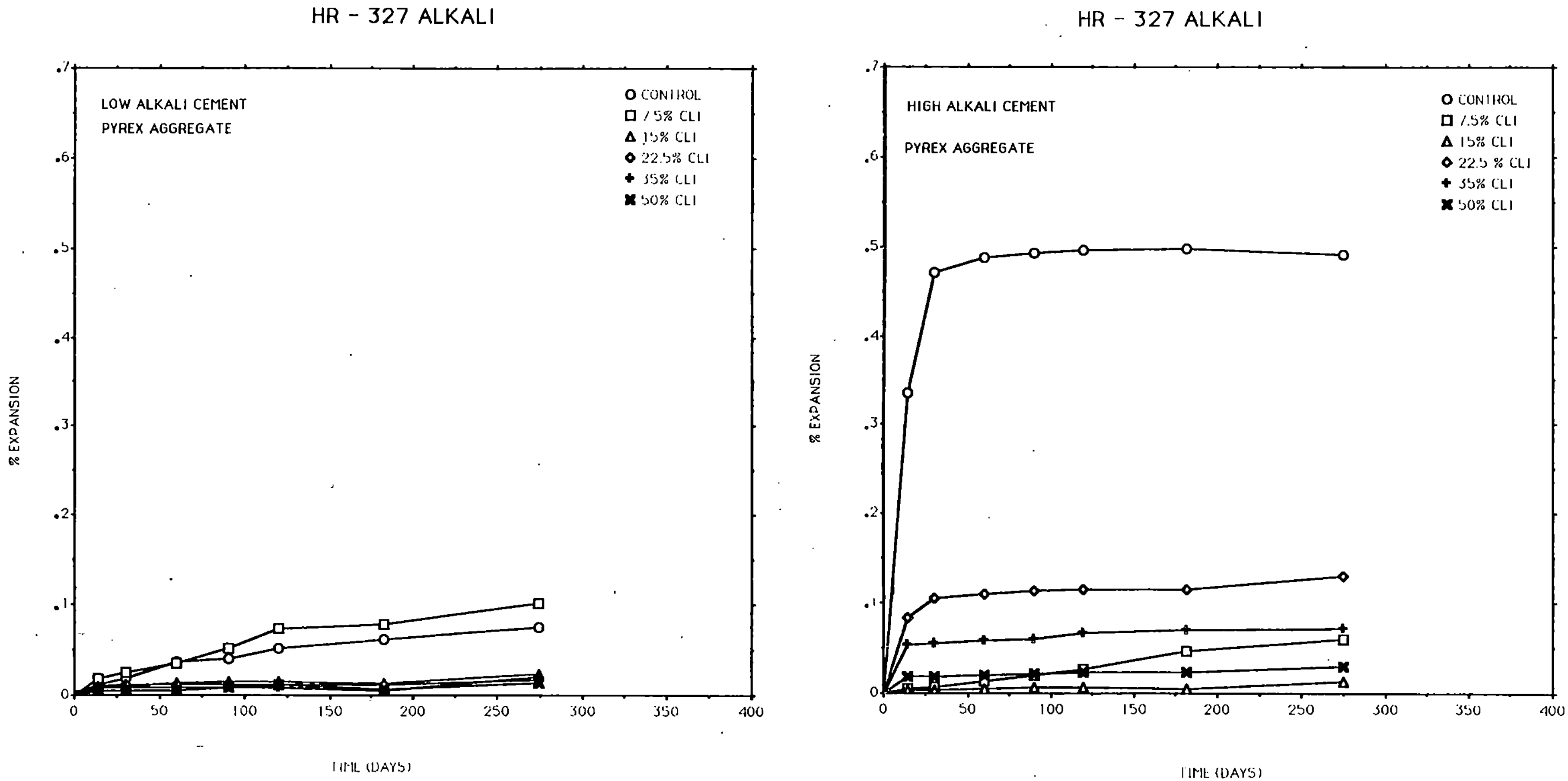


Figure 21. Alkali-reactivity test results for mortars containing Clinton fly ash and Pyrex glass aggregate.

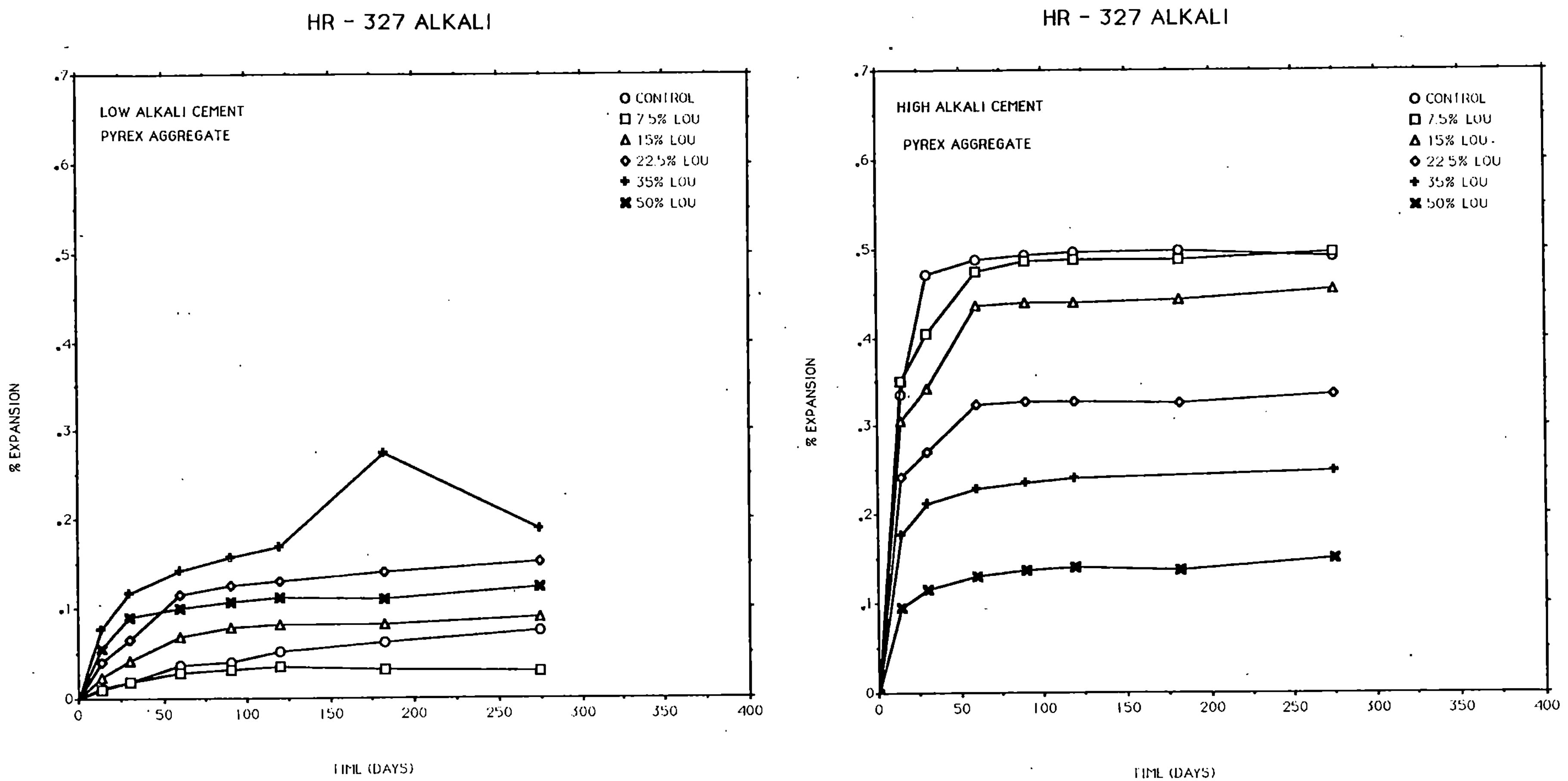


Figure 22. Alkali-reactivity test results for mortars containing Louisa fly ash and Pyrex glass aggregate.

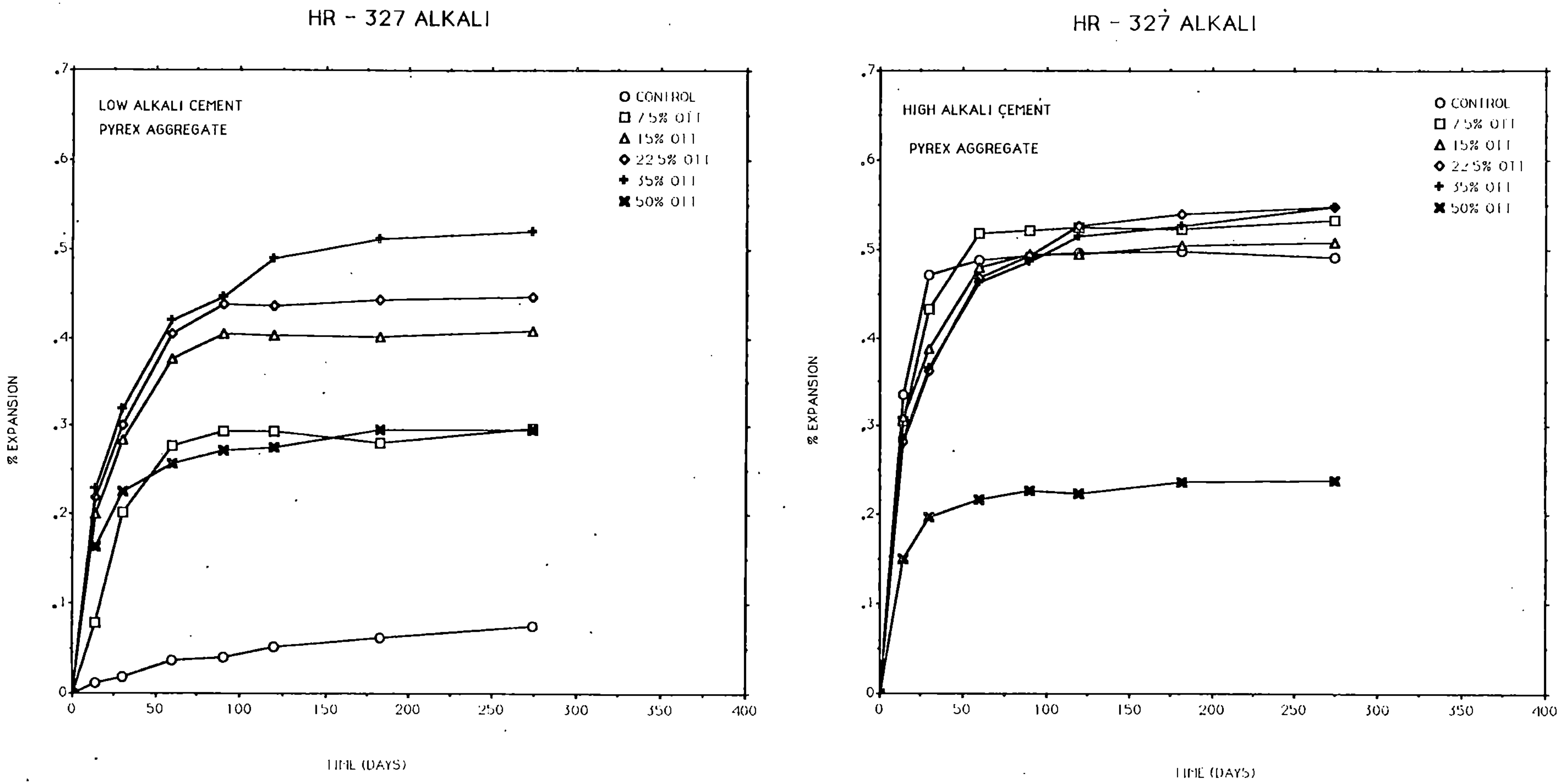


Figure 23. Alkali-reactivity test results for mortars containing Ottumwa fly ash and Pyrex glass aggregate.

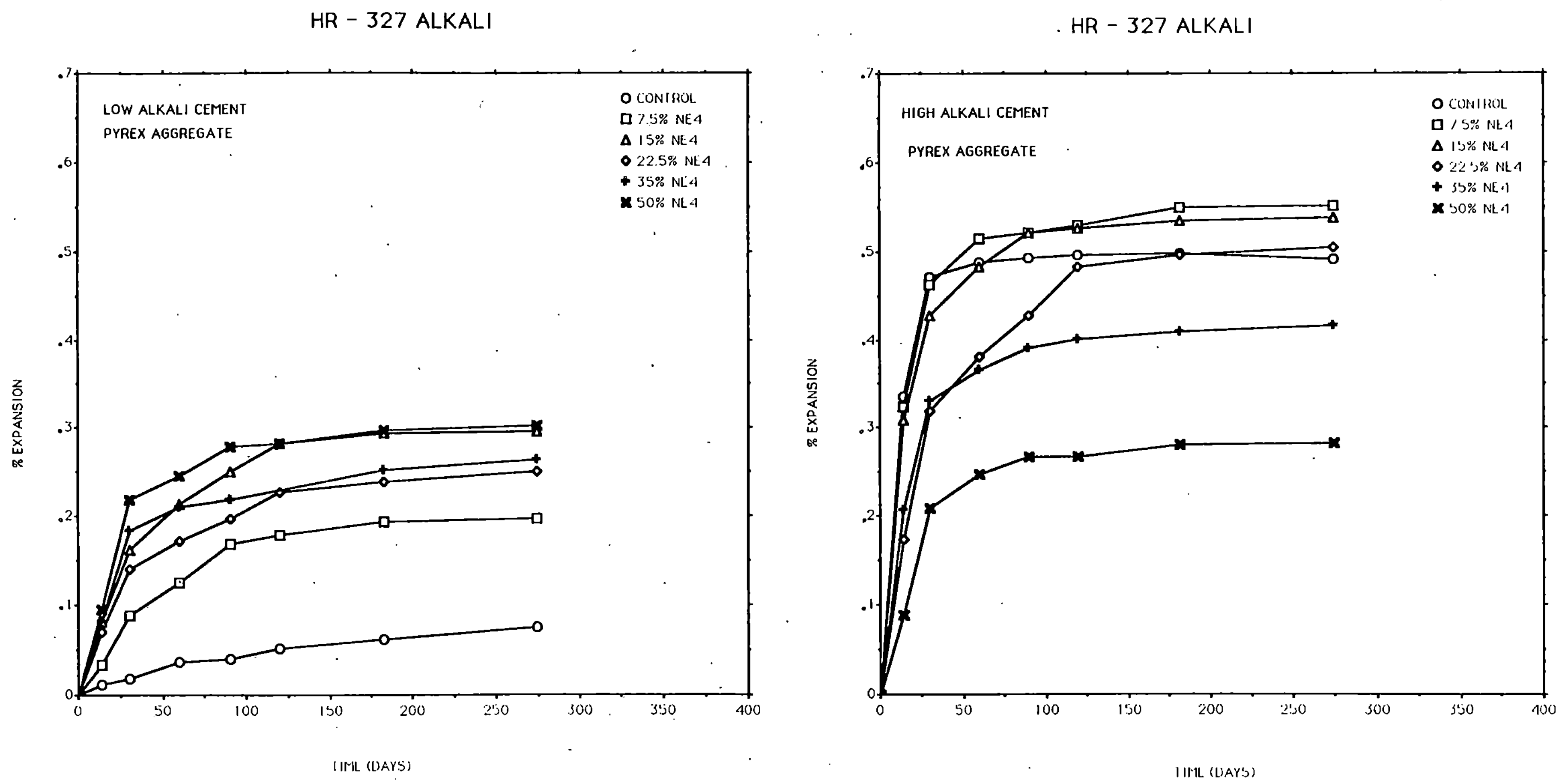


Figure 24. Alkali-reactivity test results for mortars containing Neal 4 fly ash and Pyrex glass aggregate.

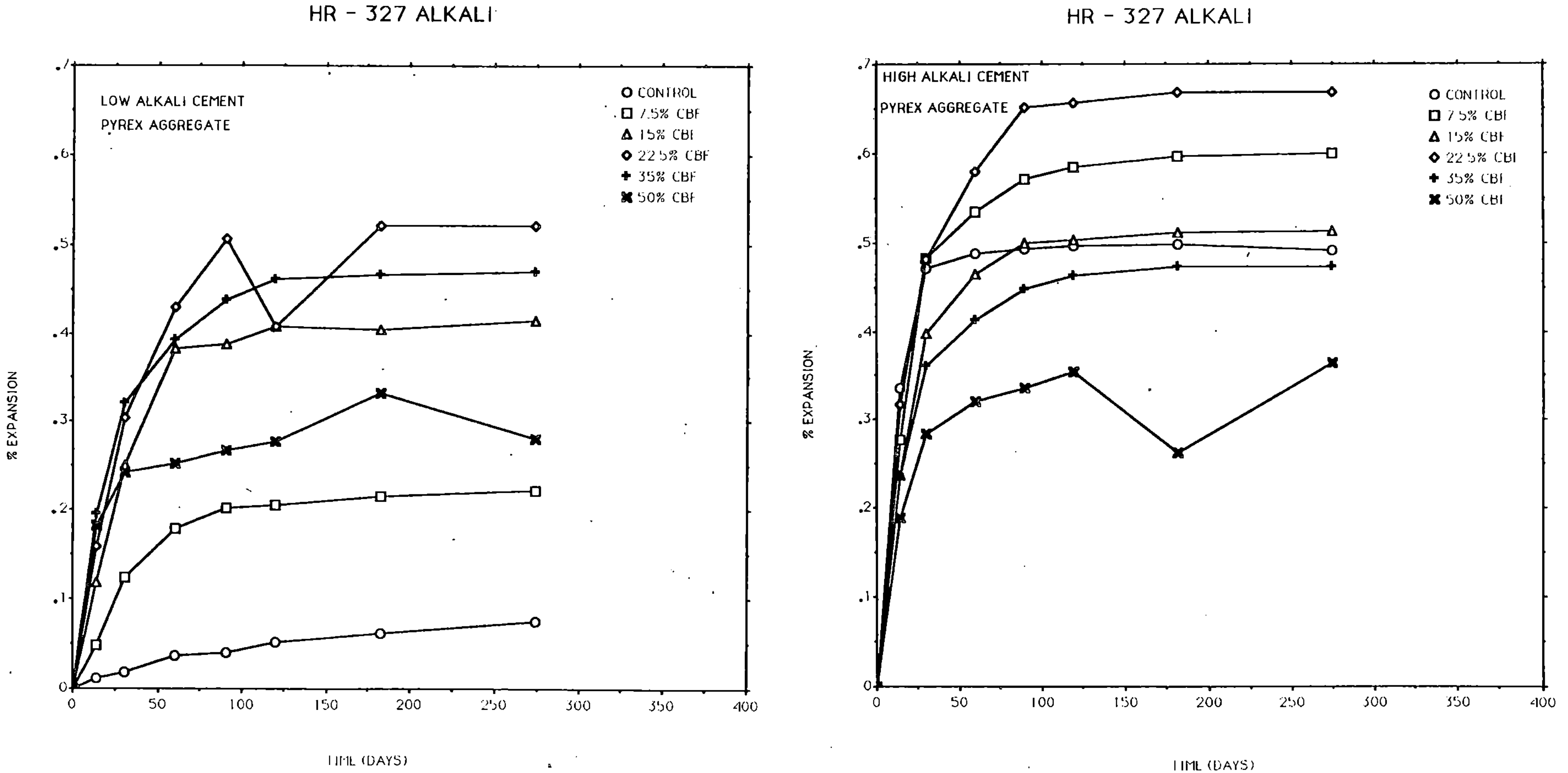


Figure 25. Alkali-reactivity test results for mortars containing Council Bluffs fly ash and Pyrex glass aggregate.

Figures 26 through 30 depict the test results obtained from mortar specimens containing the Class 5 aggregate. None of the mortar specimens exceeded the 0.10 percent expansion criterion at six months. However, specimens containing high alkali cement in combination with either Council Bluffs or Ottumwa fly ash, did approach the 0.10 percent expansion limit (see Figures 28 and 30).

Test results obtained from specimens containing the standard sand aggregate are shown in Figures 31 through 35. Again, none of the mortar specimens that were studied exceeded the six month expansion criterion of 0.10 percent.

Several of the test specimens containing the Class 5 and standard sand aggregates appeared to exhibit some rather abrupt expansive tendencies after about three months of exposure to the test environment. Also, it was not uncommon to observe specimen expansion increasing with increasing fly ash replacement. This trend was not consistent with the test results from the Pyrex aggregate study, nor did it seem restricted to only the specimens containing high alkali cement. Hence, we may be observing specimen expansion that is not related to alkali-silica reaction. Such a phenomenon has been suggested by Johnston [5], and may be very evident in the test specimens exhibiting low expansions (i.e., in the 0 to 0.05 percent range). All of the Class C fly ashes that were used in this study did contain periclase (i.e., MgO) and the delayed hydration of this compound could contribute to the expansion of the mortar specimens. A series of test specimens will be made in Phase III of this project to evaluate this potential flaw in the current test method.

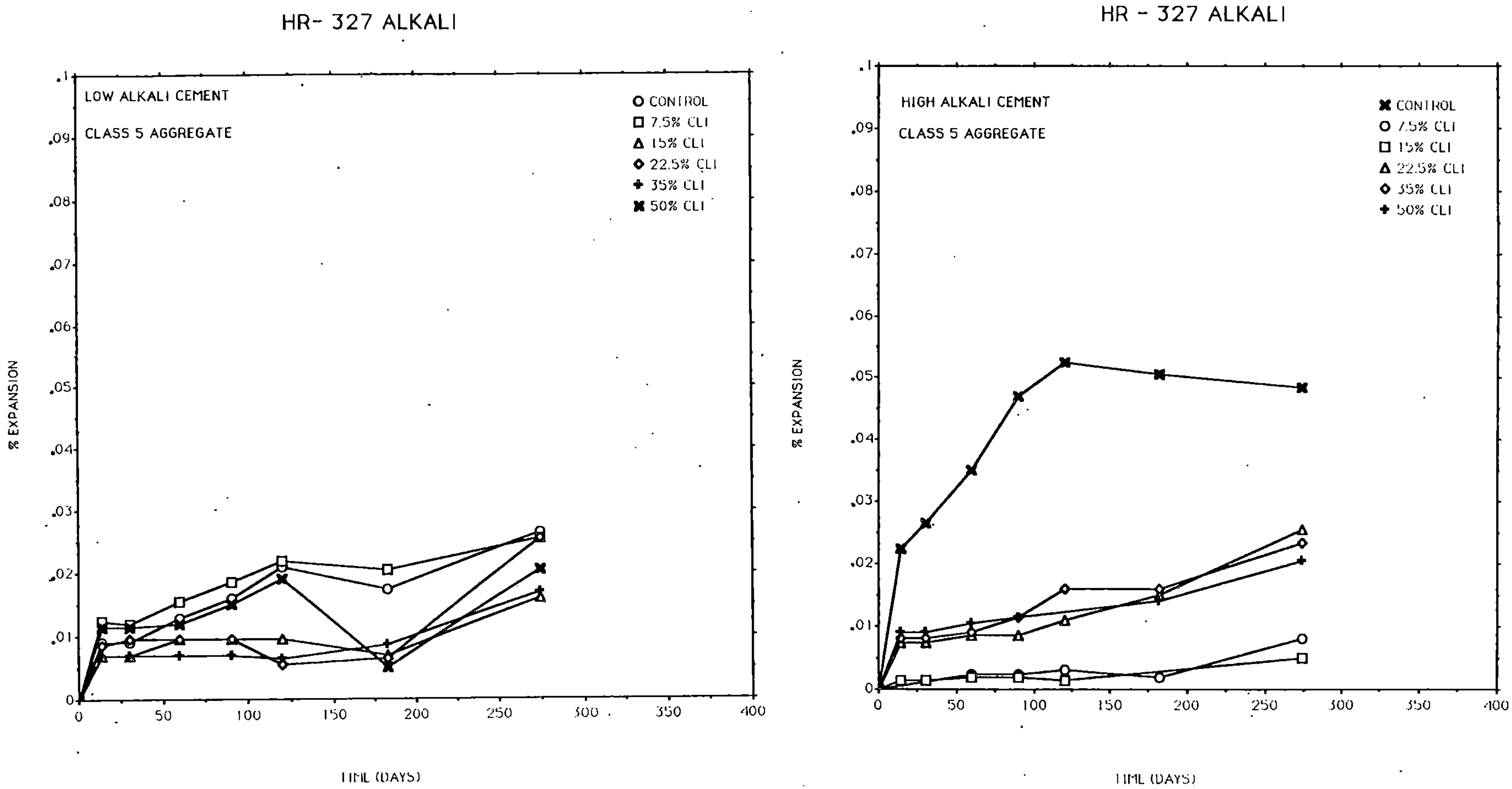


Figure 26. Alkali-reactivity test results for mortars containing Clinton fly ash and Class 5 aggregate.

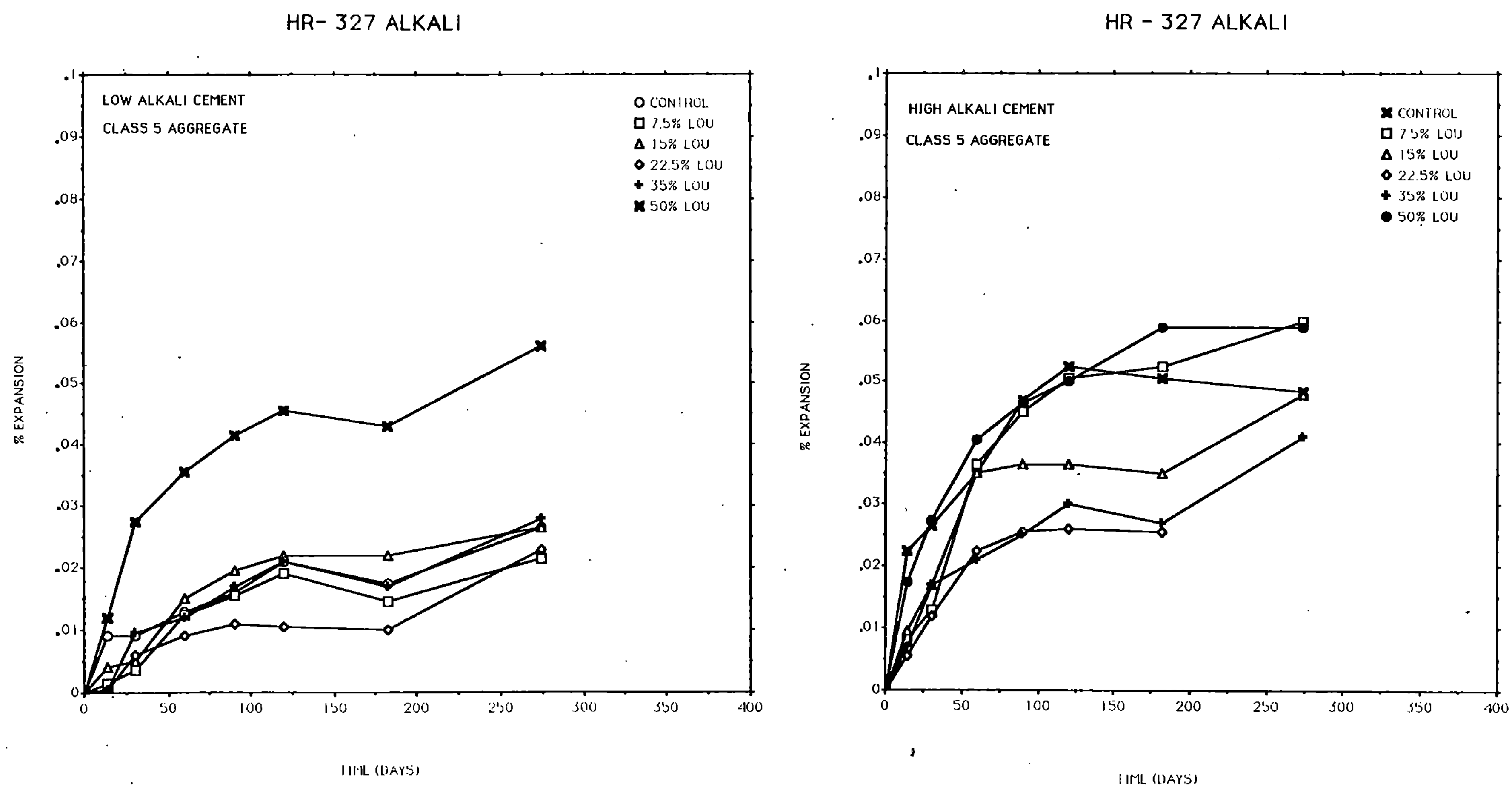


Figure 27. Alkali-reactivity test results for mortars containing Louisa fly ash and Class 5 aggregate.

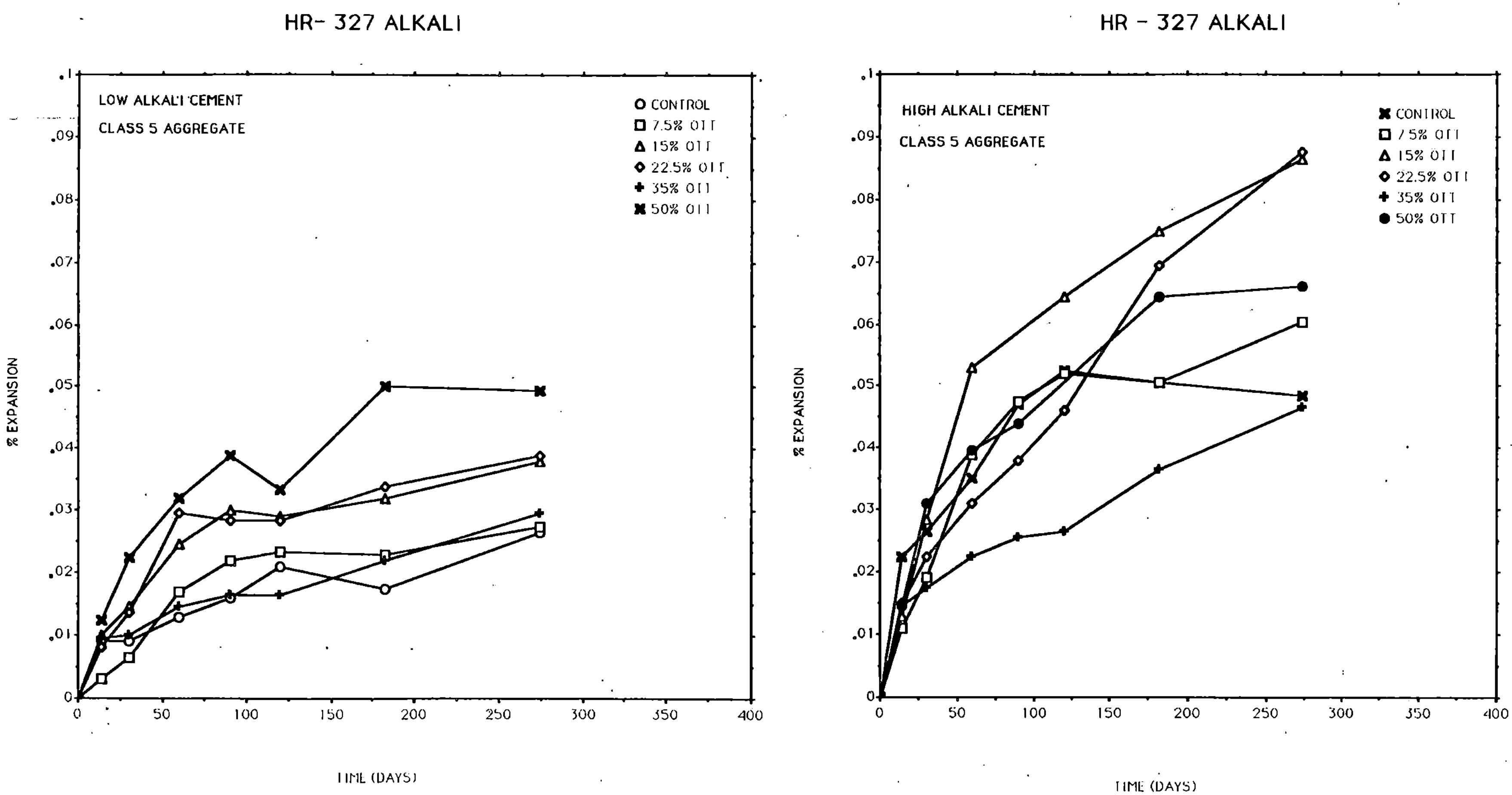


Figure 28. Alkali-reactivity test results for mortars containing Ottumwa fly ash and Class 5 aggregate.

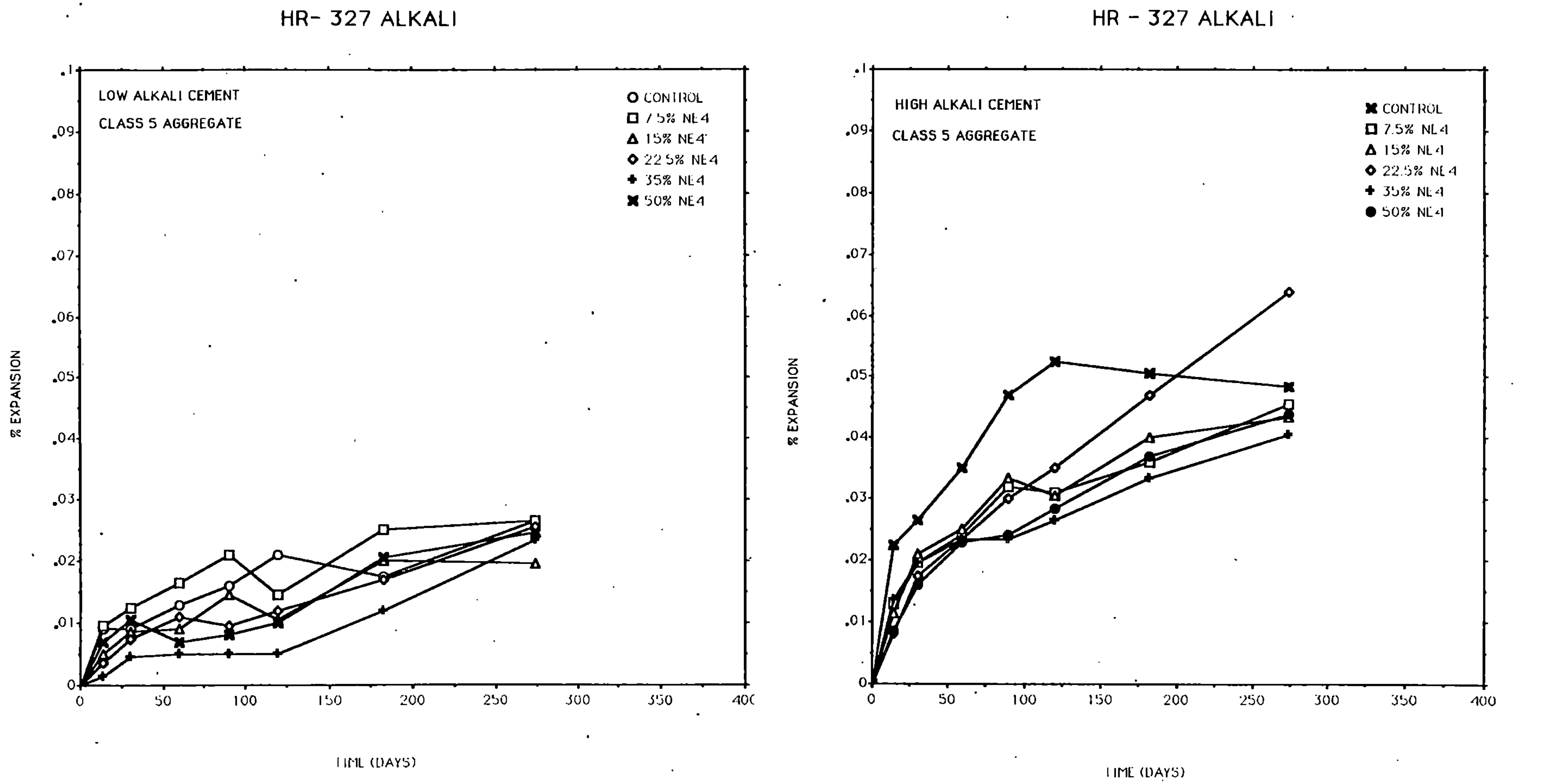


Figure 29. Alkali-reactivity test results for mortars containing Neal 4 fly ash and Class 5 aggregate.

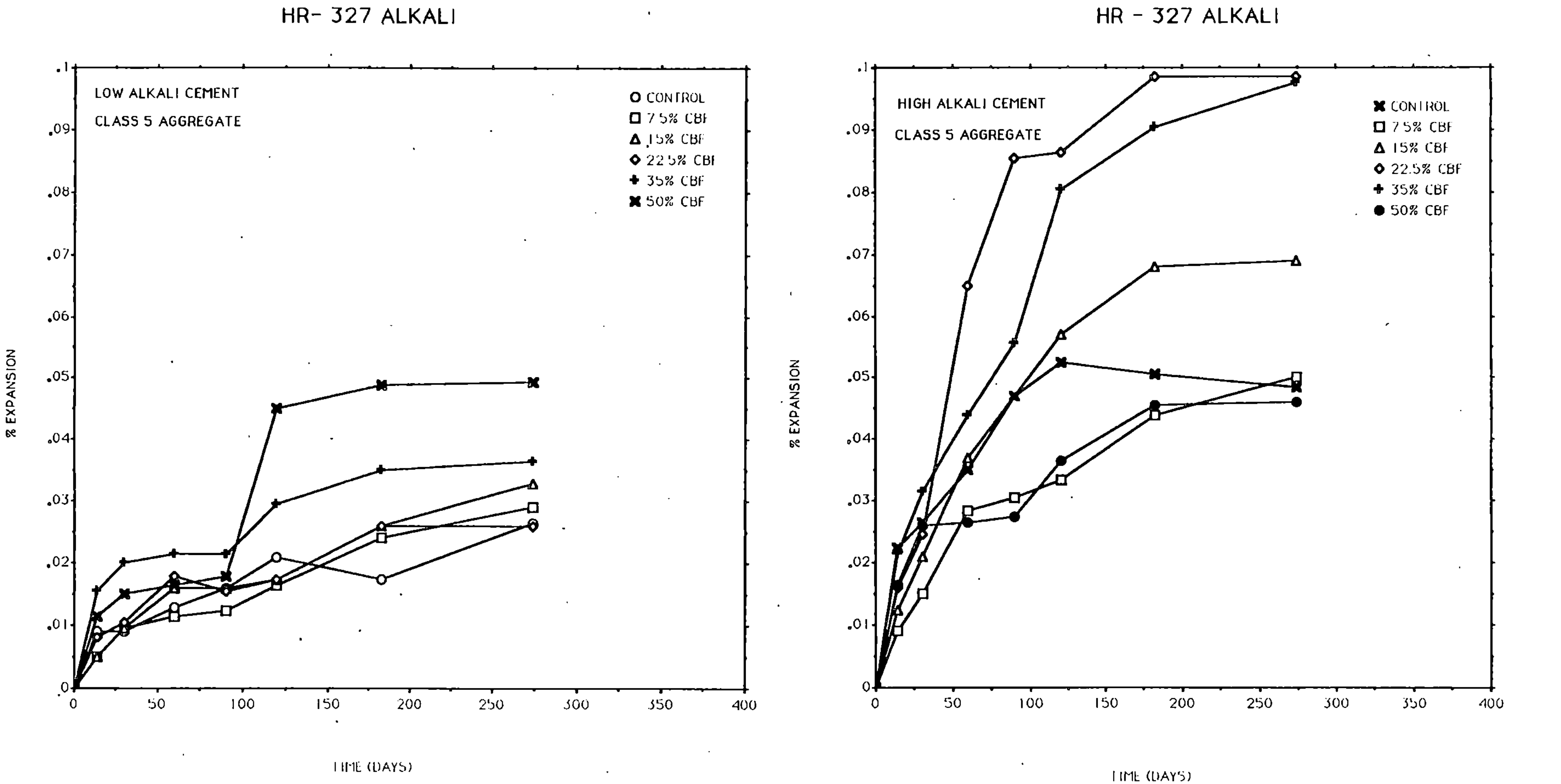


Figure 30. Alkali-reactivity test results for mortars containing Council Bluffs fly ash and Class 5 aggregate.

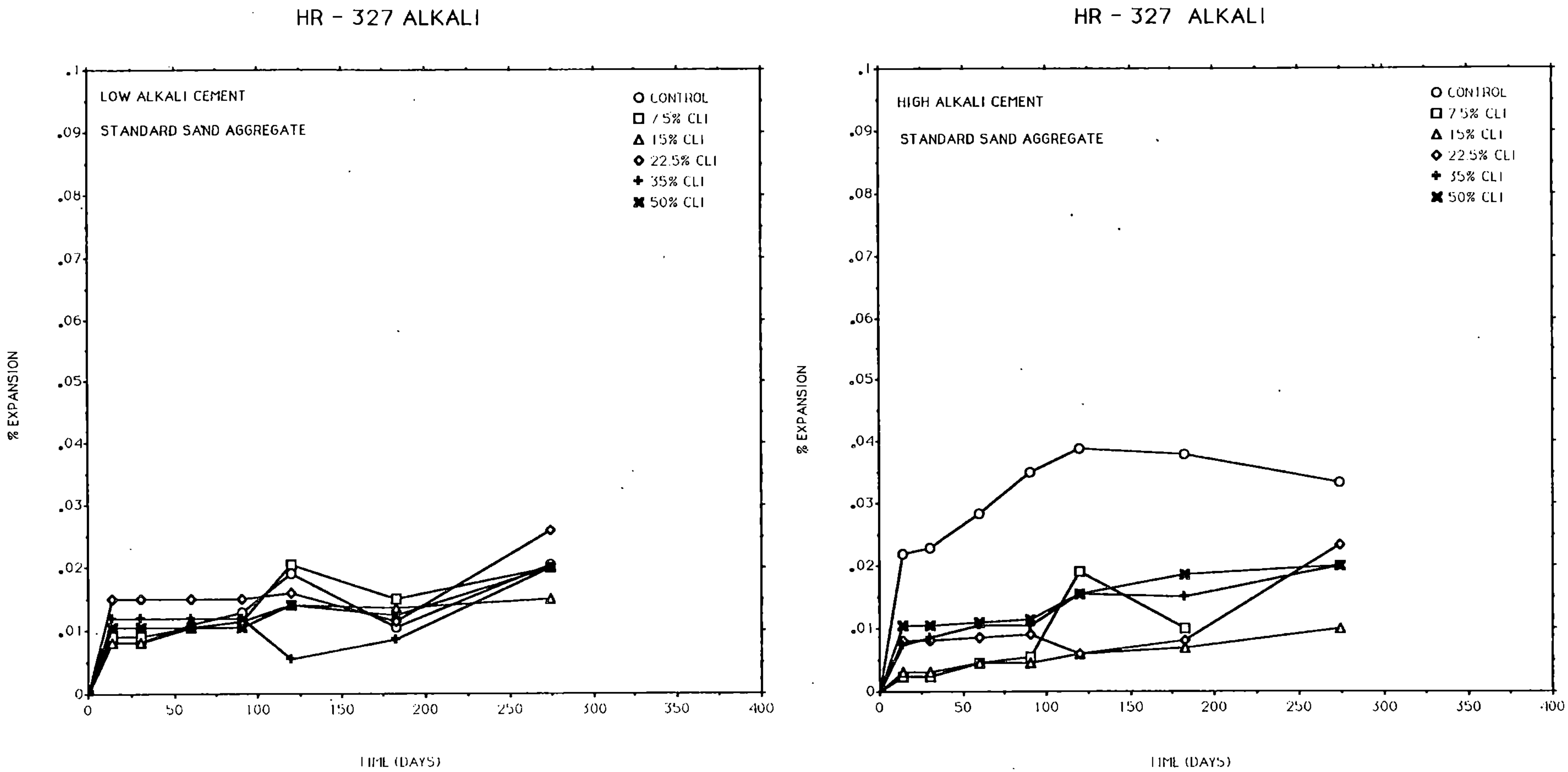


Figure 31. Alkali reactivity test results for mortars containing Clinton fly ash and C 109 standard sand.

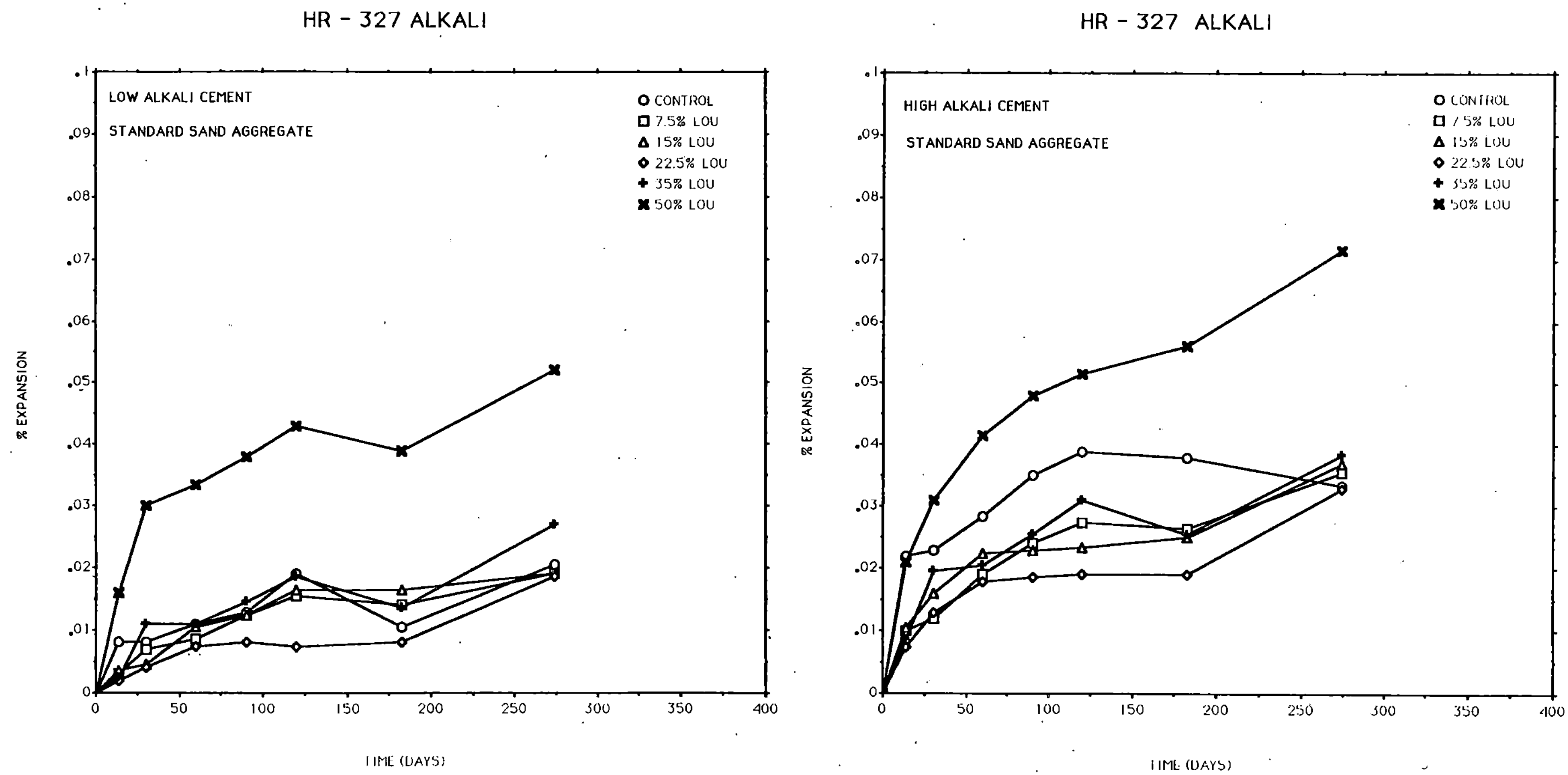


Figure 32. Alkali reactivity test results for mortars containing Louisa fly ash and C 109 standard sand.

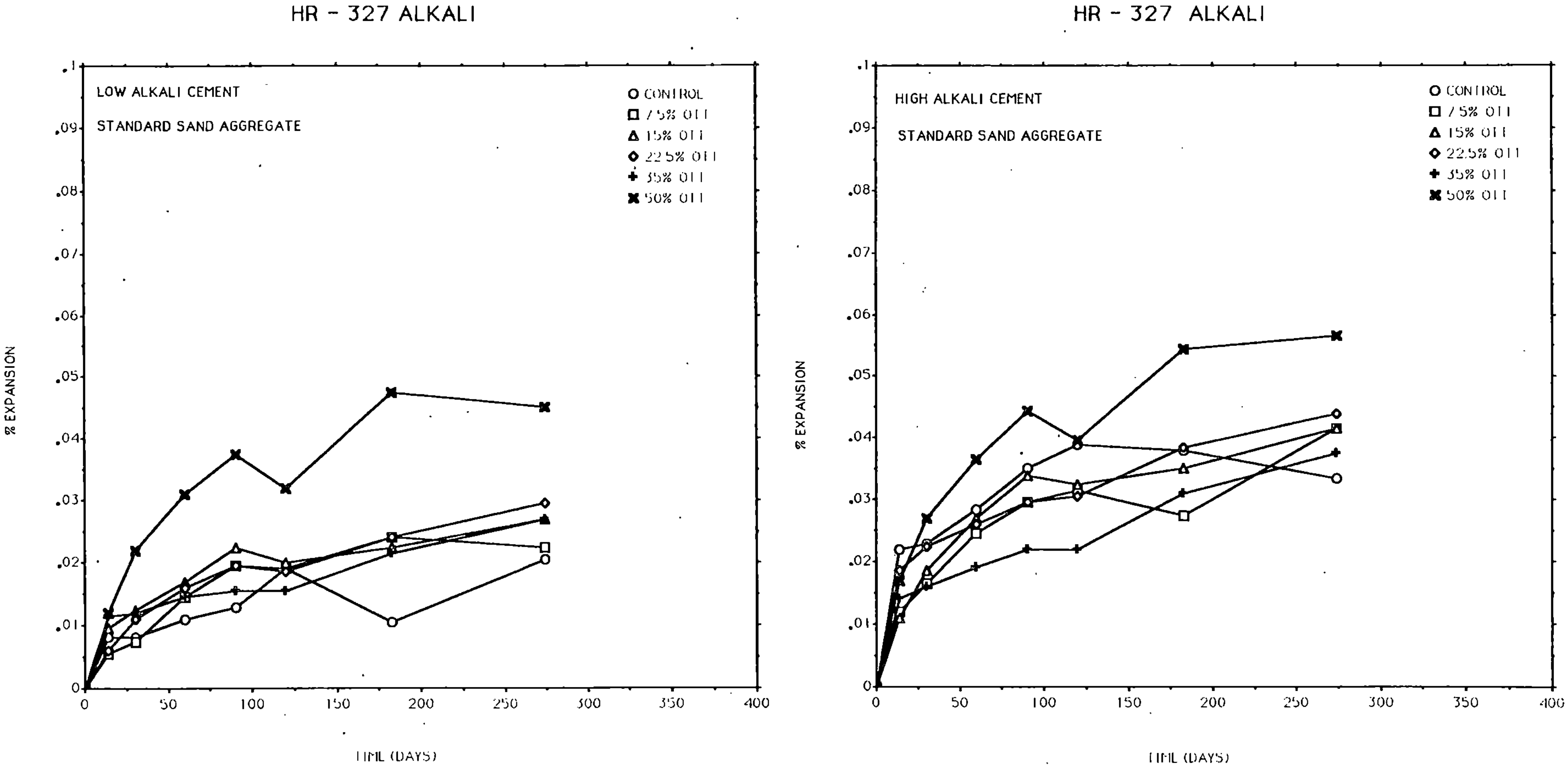
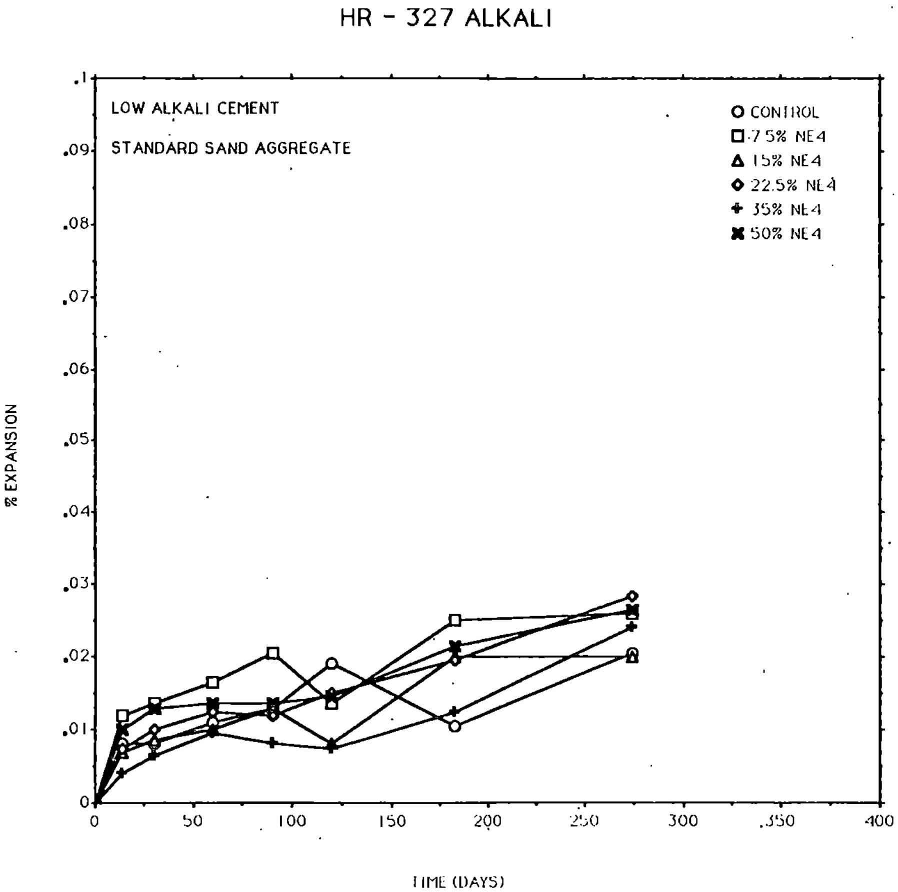


Figure 33. Alkali reactivity test results for mortars containing Ottumwa fly ash and C 109 standard sand.



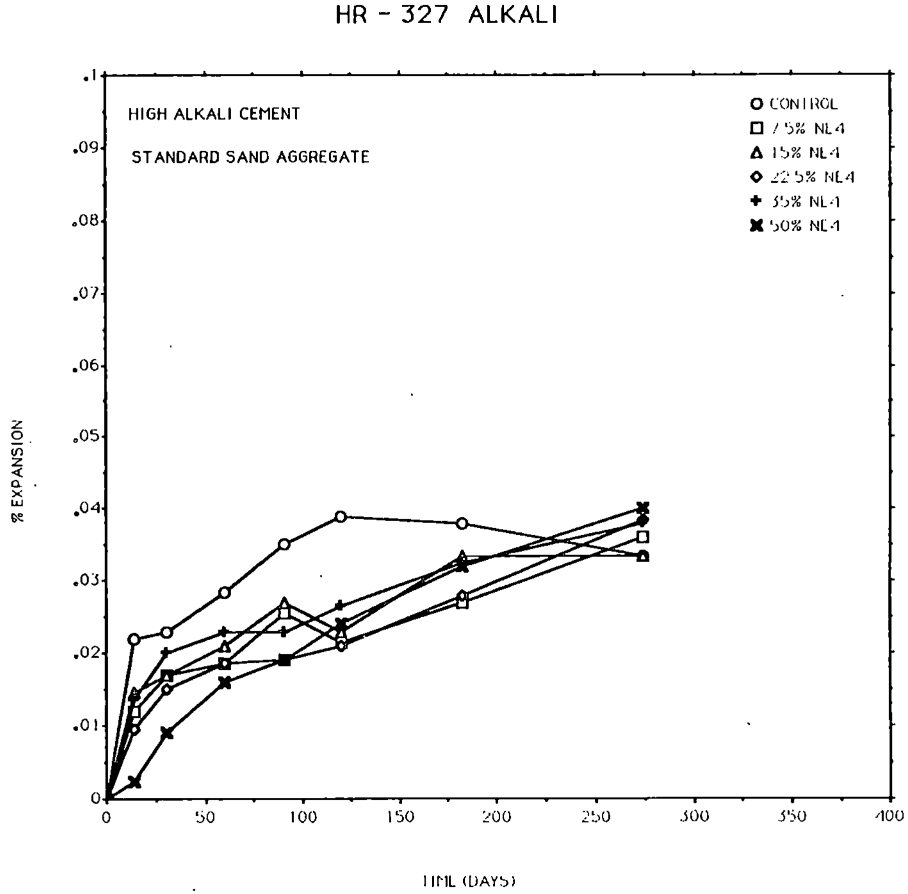
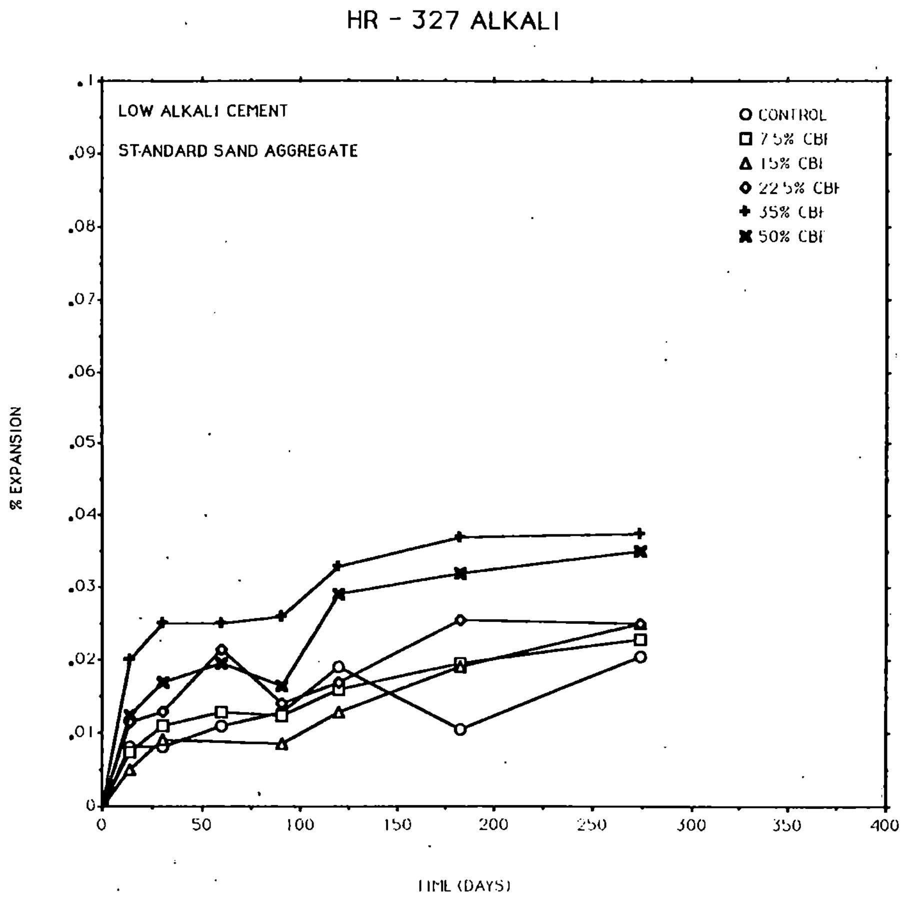


Figure 34. Alkali reactivity test results for mortars containing Neal 4 fly ash and C 109 standard sand.



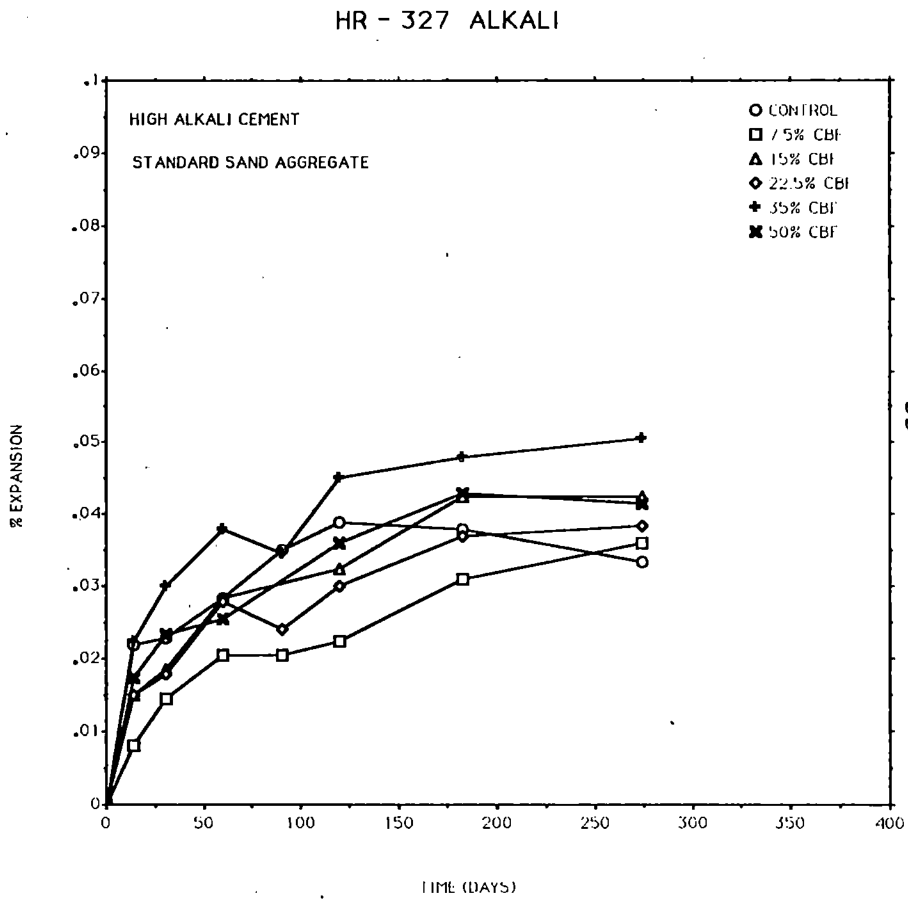


Figure 35. Alkali reactivity test results for mortars containing Council Bluffs fly ash and C 109 standard sand.

SUMMARY AND FURTHER DISCUSSION

In summary, much of the second year of this project has been spent monitoring the specimens that were made during Phase I. Several of the experiments that had been initiated are currently yielding only marginal response to the exposure conditions; and hence, it is simply too early to predict the outcome of the experiments. This is especially true for the concrete specimens that are being exposed to sulfate solutions.

Also, additional specimens have been molded for the concrete and mortar bar studies and have recently been subjected to sulfate bearing solutions. More specimens are being planned for casting during the 1992 calendar year. These last series of test specimens should complete the work plan that was described in the original research proposal.

The preliminary results of the ASTM C 1012 mortar bar studies have indicated that the sulfate resistance of test specimens tend to decrease with increasing bulk analytical CaO content of the fly ash (see Figure 36). Note in Figure 36, that all of the mortar specimens containing fly ash, with the exception of the Council Bluffs ash (29.1 percent CaO), increased the sulfate resistance of specimens containing Type I portland cement (as compared to Type I control mortar). This is especially evident when considering the results of mortar specimens subjected to the synthetic deicer soak solution. However, the overall trend indicated in Figure 36 is definitely downward. Other researchers have published similar test results [6, 7], although they may have presented the results in a different format. However, a problem arises from the fact that this relationship does very little to describe the mechanism by which fly ash causes the specimens to become prone to sulfate attack.

The chemical information presented in this report suggests that specimen expansion is related to the conversion of monosulfoaluminate to ettringite and/or the conversion of portlandite to gypsum. Hence, these results indicate that potential reaction mechanisms should be related to the calcium, aluminum or sulfate content of the pore solution of the test specimens. Since the system is composed primarily of portland cement (about 65 percent CaO) and is immersed in a

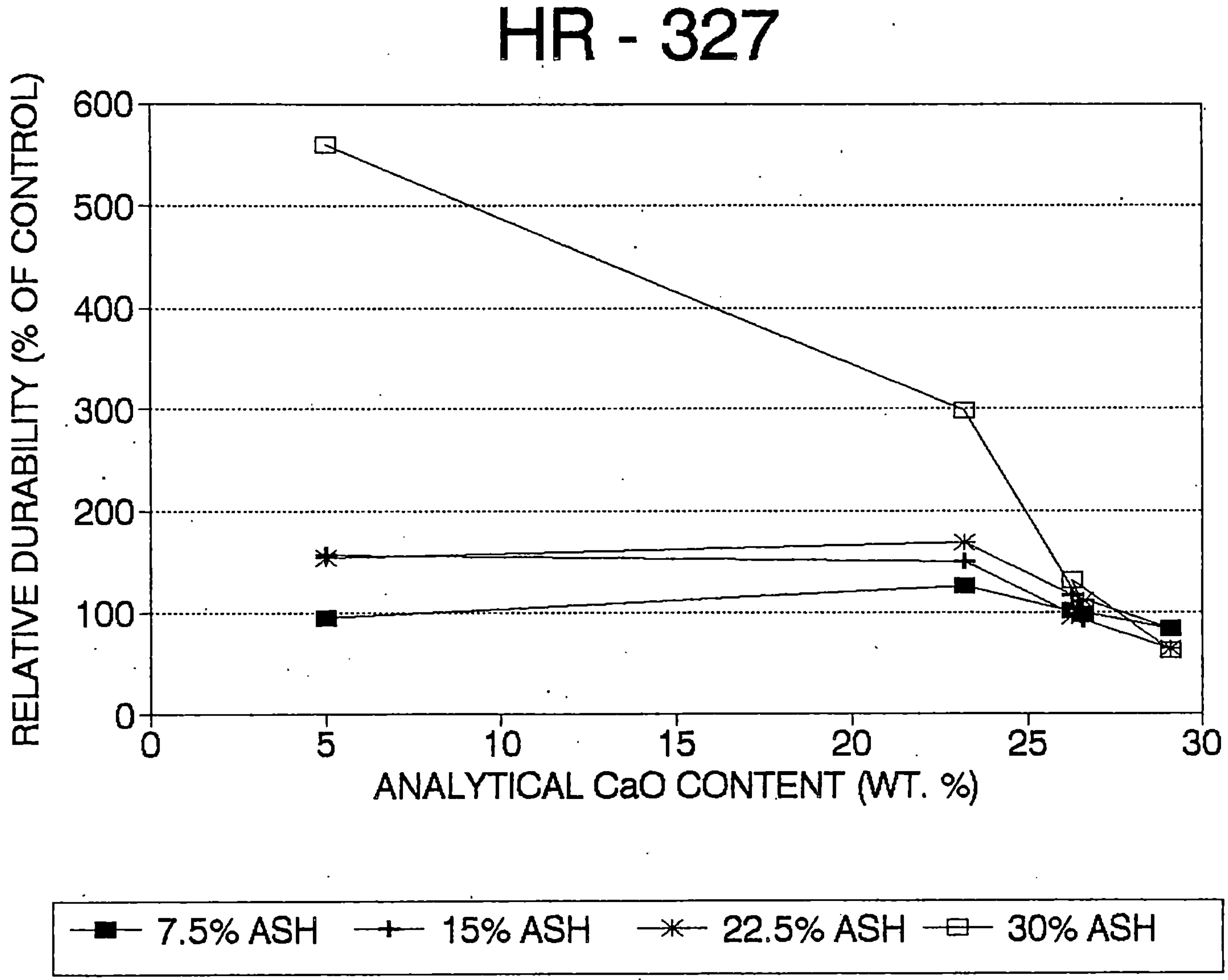


Figure 36. Relative sulfate durability versus analytical CaO content of the fly ashes used in this study (mortar specimens made with Type I cement).

solution containing 5 percent sodium sulfate it seems odd that a small change in fly ash content (i.e., 0 to 30 percent, by weight) could significantly perturb either the calcium or sulfur content of the pore solution. Fly ashes can, however, donate a significant amount of aluminum to the pore solution because, as we have shown in previous research [3], that is the nature of their self-cementitious behavior. Hence, in theory, one would suspect that increasing amounts of "available" aluminum in fly ash should lead to a decrease in sulfate resistance. The major problem with this concept is the difficulty in defining "available" aluminum. However, a very rough approximation of "available" aluminum content can be made by using the acid solubility of the bulk ash in conjunction with the chemical analyses of the various fly ashes before and after acid extraction. The results obtained from such a calculation are shown in Figure 37. The trend indicated in Figure 37 is very similar to the one that was observed in Figure 36. Obviously, the experimental procedure that will be used to determine the "available" aluminum content of a given fly ash needs considerable refinement before it can be used as a simple criterion for predicting the sulfate resistance of fly ash-cement mixtures.

The preliminary results of the alkali-reactivity tests described in this report are in excellent agreement with those reported in earlier work conducted by Jones [4]. In fact, the preliminary results, which consist of information collected over a duration of about six to nine months, verify both the observations and conclusions made by Jones [4]. The test specimens are still being monitored and results will be updated and re-evaluated as they become available. Also, this portion of the project will be broadened during Phase III to include a series of test mortars that can be used to evaluate the influence of periclase (present in the fly ash) on the expansion of the alkali-reactivity test specimens.

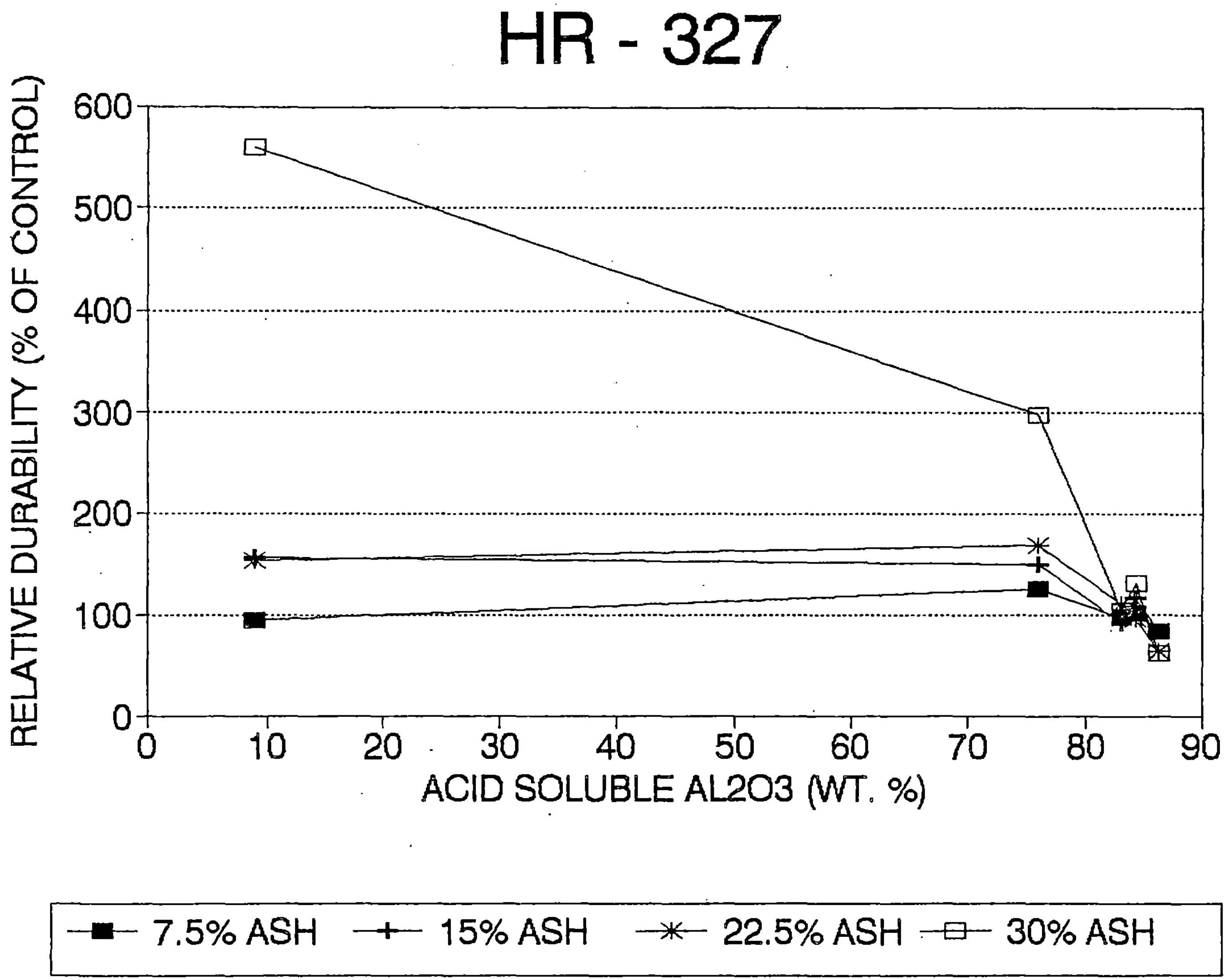


Figure 37. Relative sulfate durability versus acid soluble aluminum content of the fly ashes used in this study (mortar specimens made with Type I cement).

ACKNOWLEDGEMENTS

We would like to thank all the people who helped to contribute to this project during its second year. A special thanks to IDOT personnel who have helped to make and monitor concrete specimens. Without their help this research project would not have been possible.

REFERENCES

1. Schlorholtz, S., Bergeson, K., and Enüstün, V., Evaluation of the Chemical Durability of Iowa Fly Ash Concretes, Report for Phase I, Iowa DOT Project HR-327, March 31, 1991.

2. American Society for Testing and Materials, 1990 Annual Book of ASTM Standards Vol. 4.02, (ASTM, Philadelphia, PA, 1990).

3. Bergeson, K.L., Schlorholtz, S., and Demirel, T., Development of a Rational Characterization Method for Iowa Fly Ashes, Final Report for Iowa DOT Project HR-286, November 30, 1988.

4. Jones, K., Fly Ash Affect on Alkali-AGGREGATE REACTIVITY, Final Report MLR-88-7, Iowa Department of Transportation, June, 1989.

5. Johnston, D., Investigation of the Effects of Chemical Composition on Mortar Bar Expansion, Draft Report, South Dakota Department of Transportation, March, 1990.

6. Von Fay, F. and Pierce, J.S., Sulfate Resistance of Concretes with Various Fly Ashes, ASTM Standardization News, December, 1989.

7. Tikalsky, P.J. and Carrasquillo, R.L., Effect of Fly Ash on the Sulfate Resistance of Concrete Containing Fly Ash, Research Report 481-1, Center for Transportation Research, Bureau of Engineering Research, The University of Texas at Austin, February, 1988.

APPENDIX I

APPENDIX I (concrete studies)

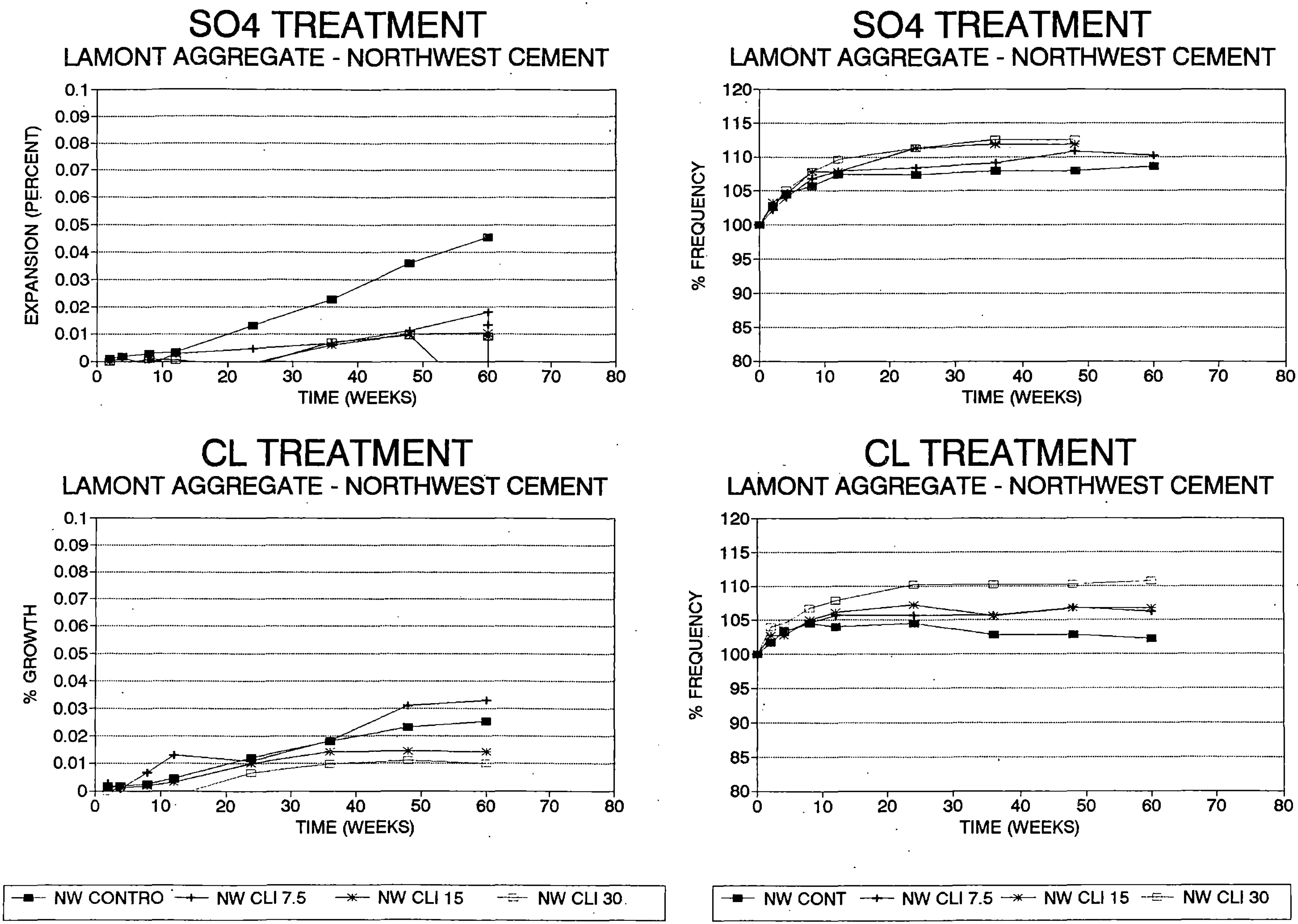


Figure 1, Appendix I. Concrete test results.

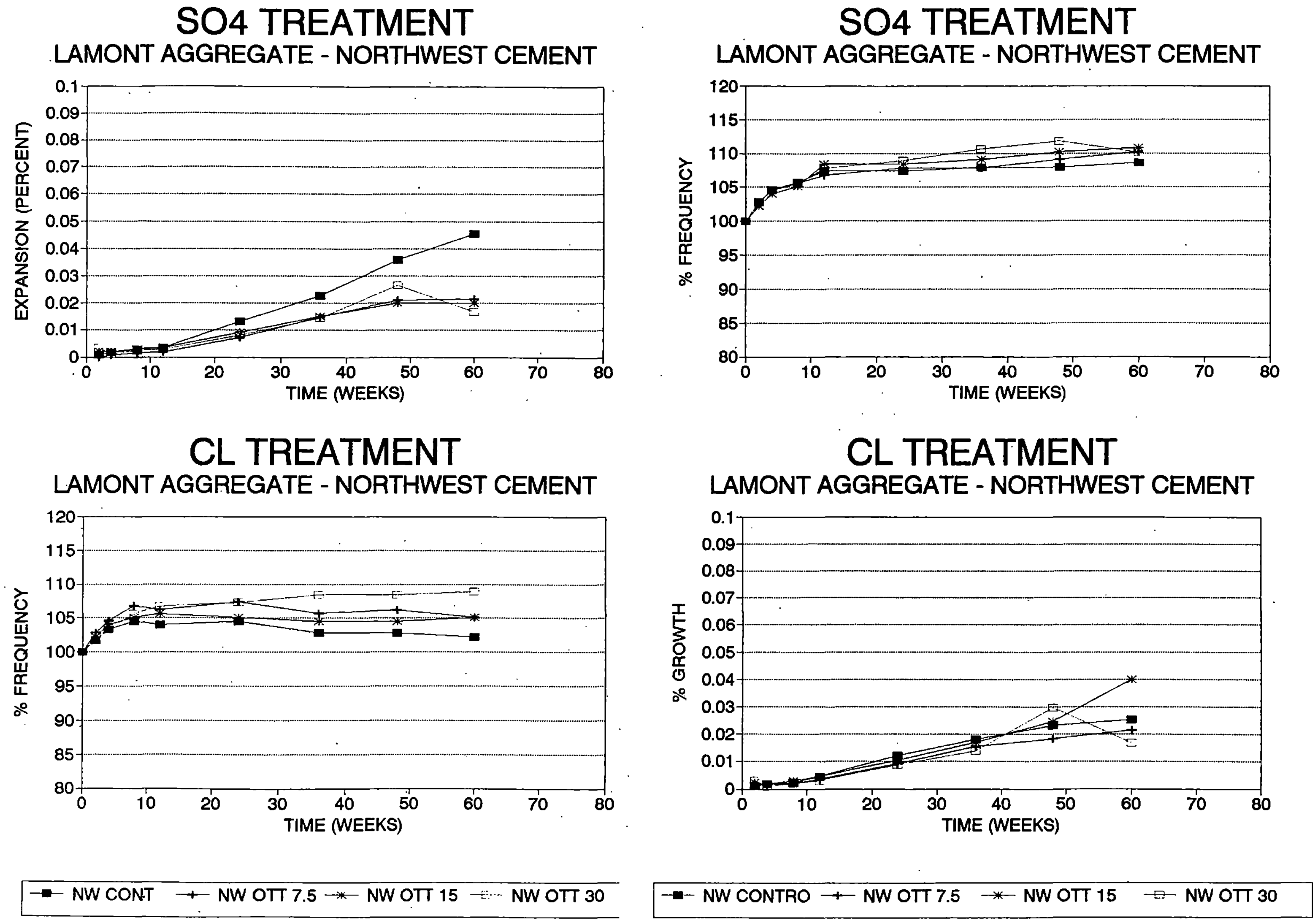


Figure 2, Appendix I. Concrete test results.

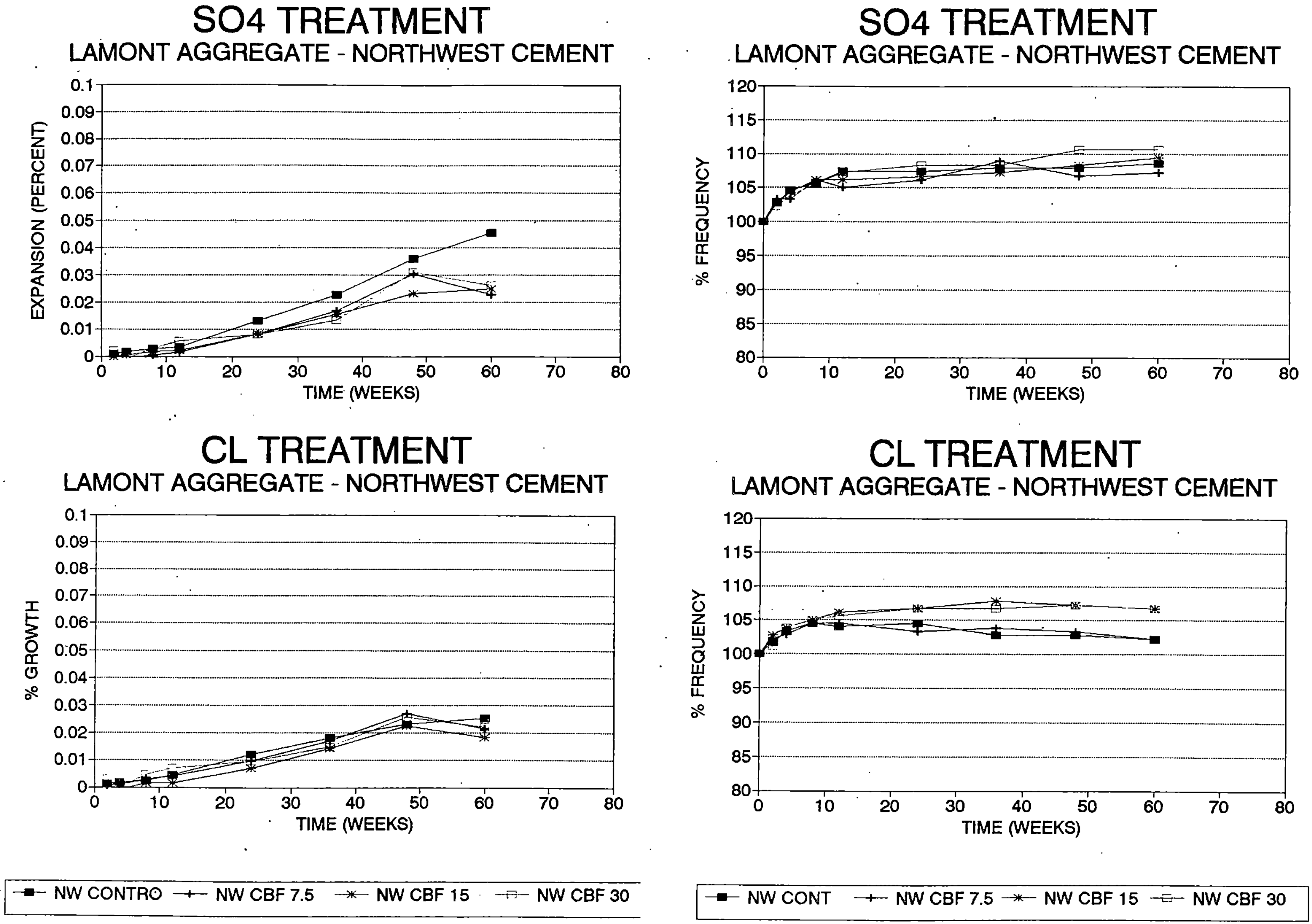


Figure 3, Appendix I. Concrete test results.

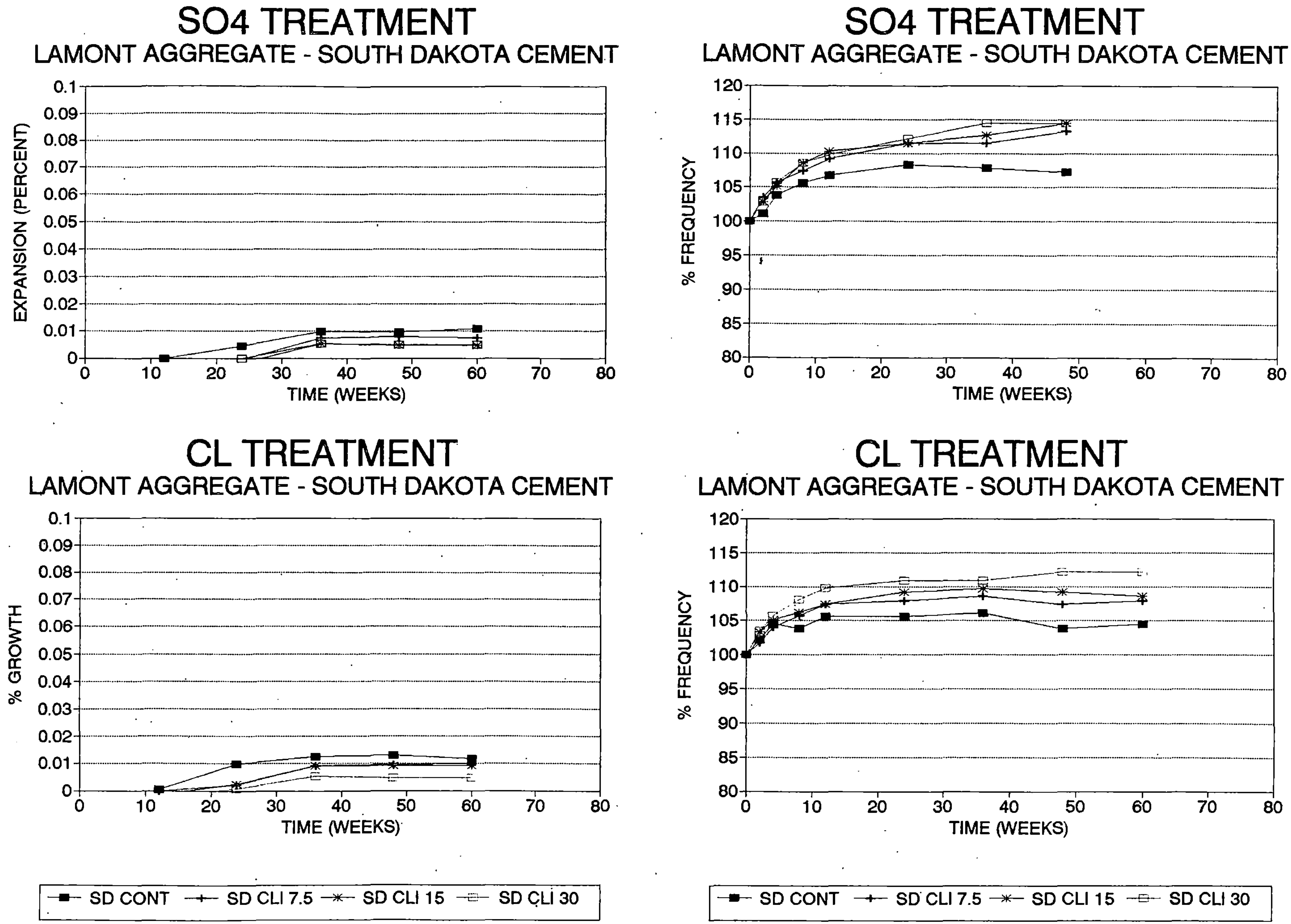


Figure 4, Appendix I. Concrete test results.

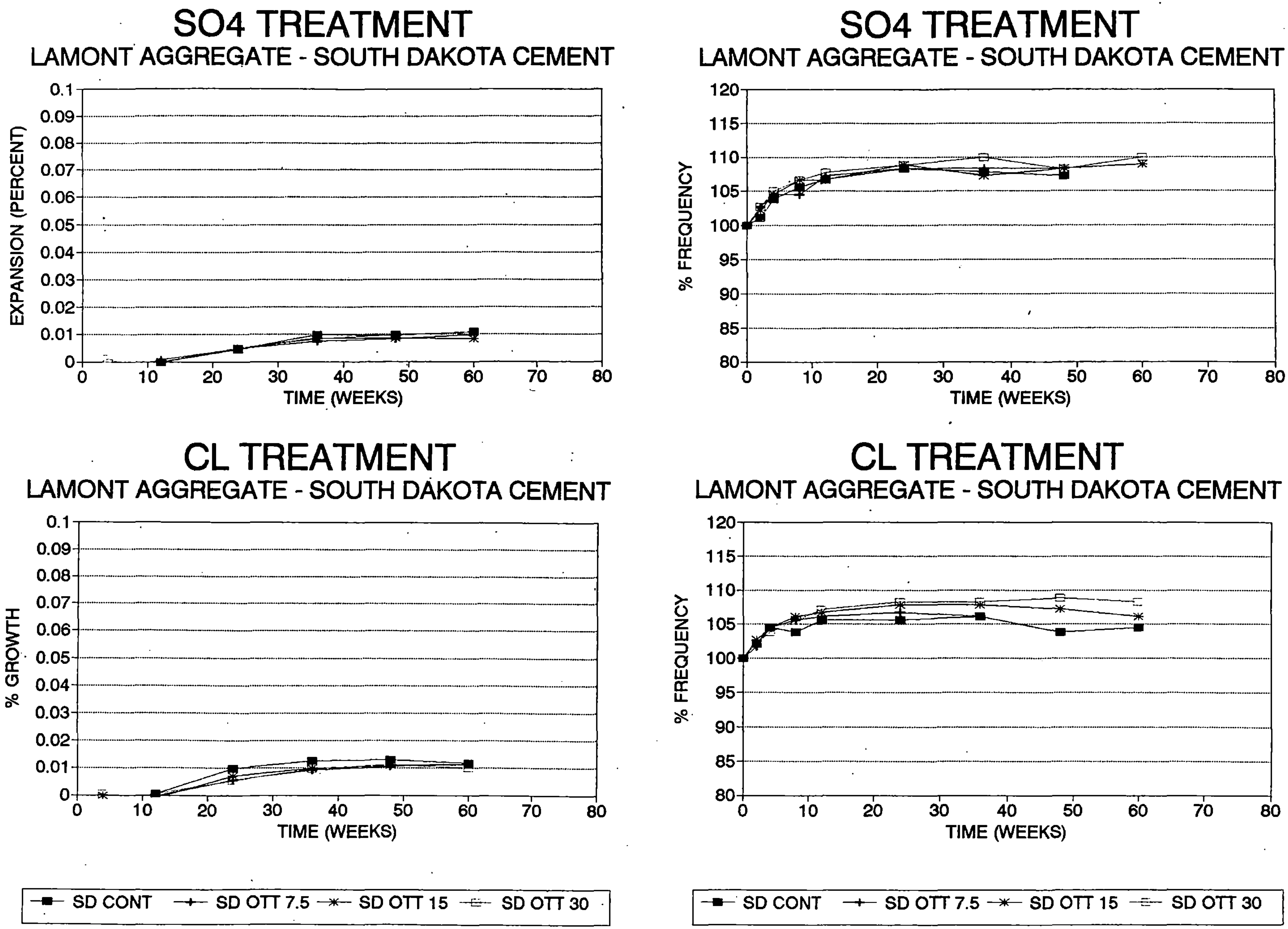
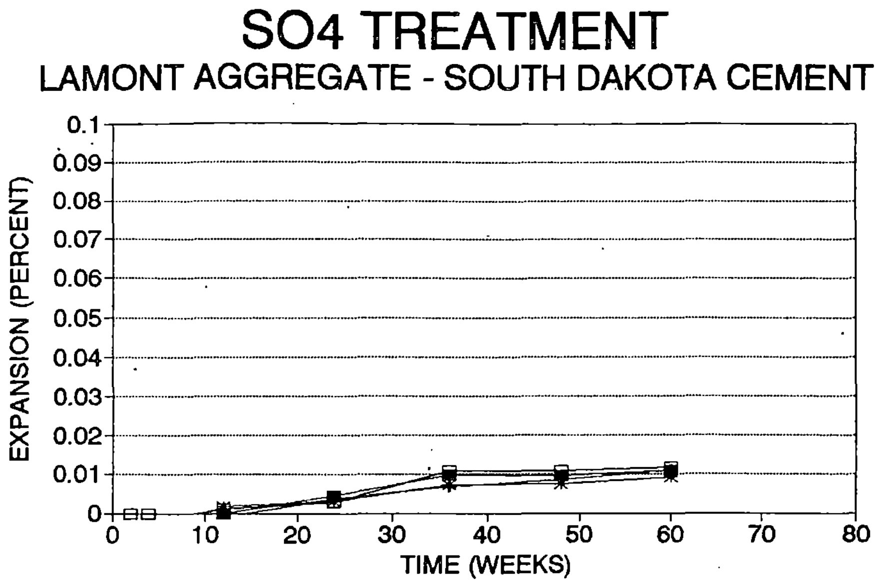
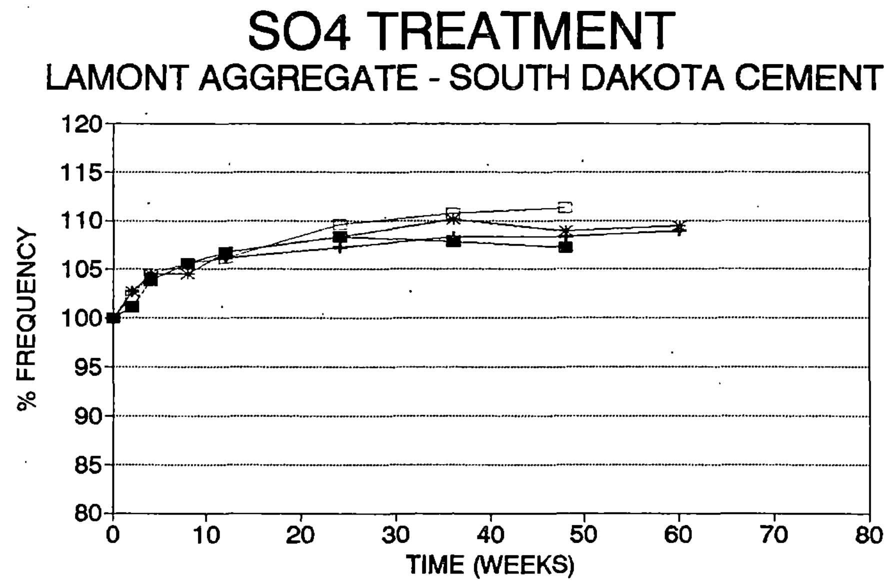
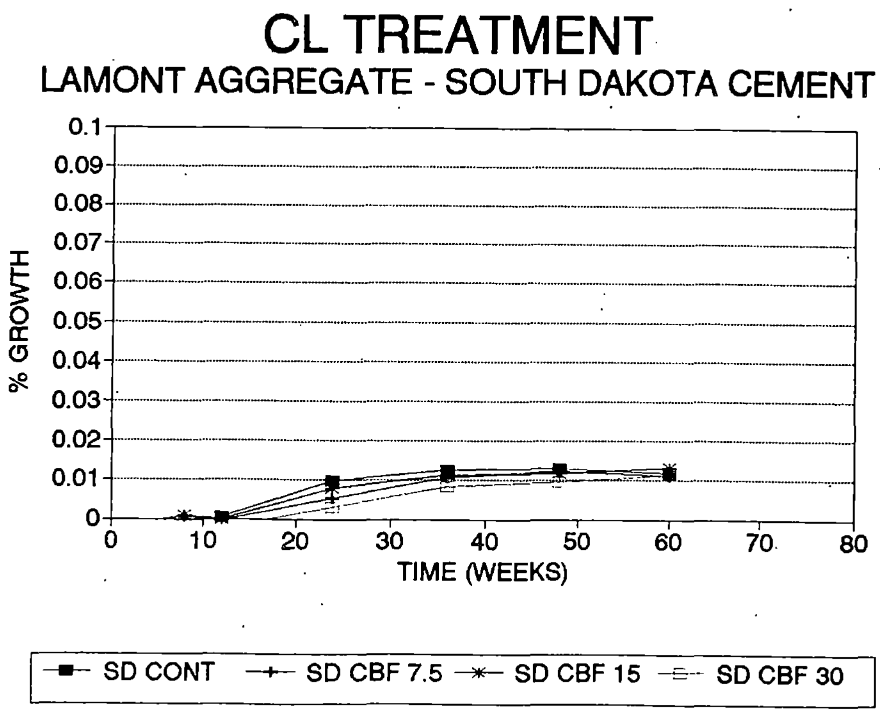


Figure 5, Appendix I. Concrete test results.







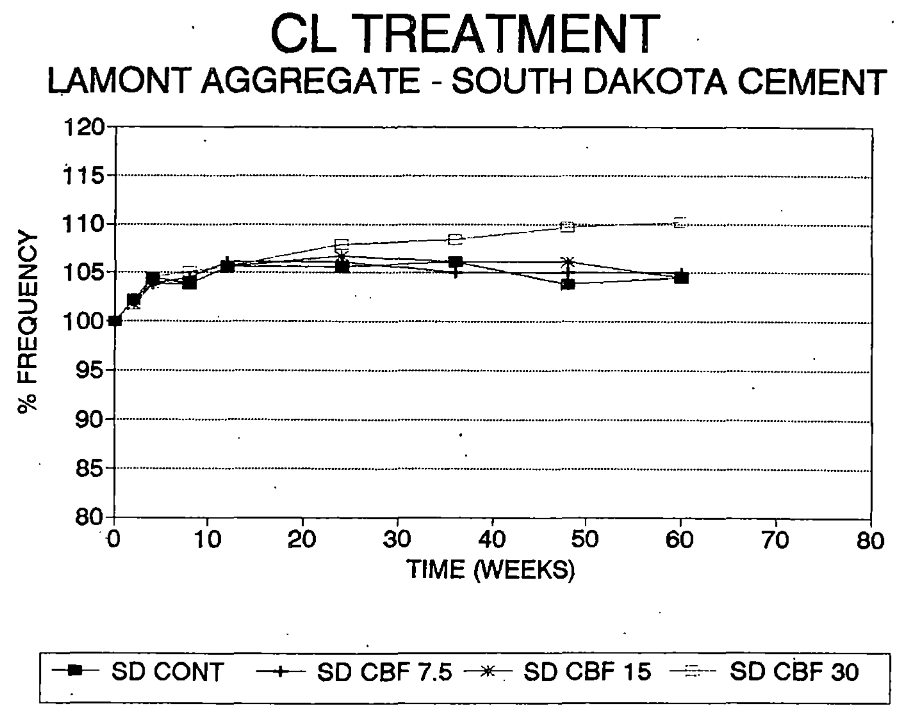


Figure 6, Appendix I. Concrete test results.

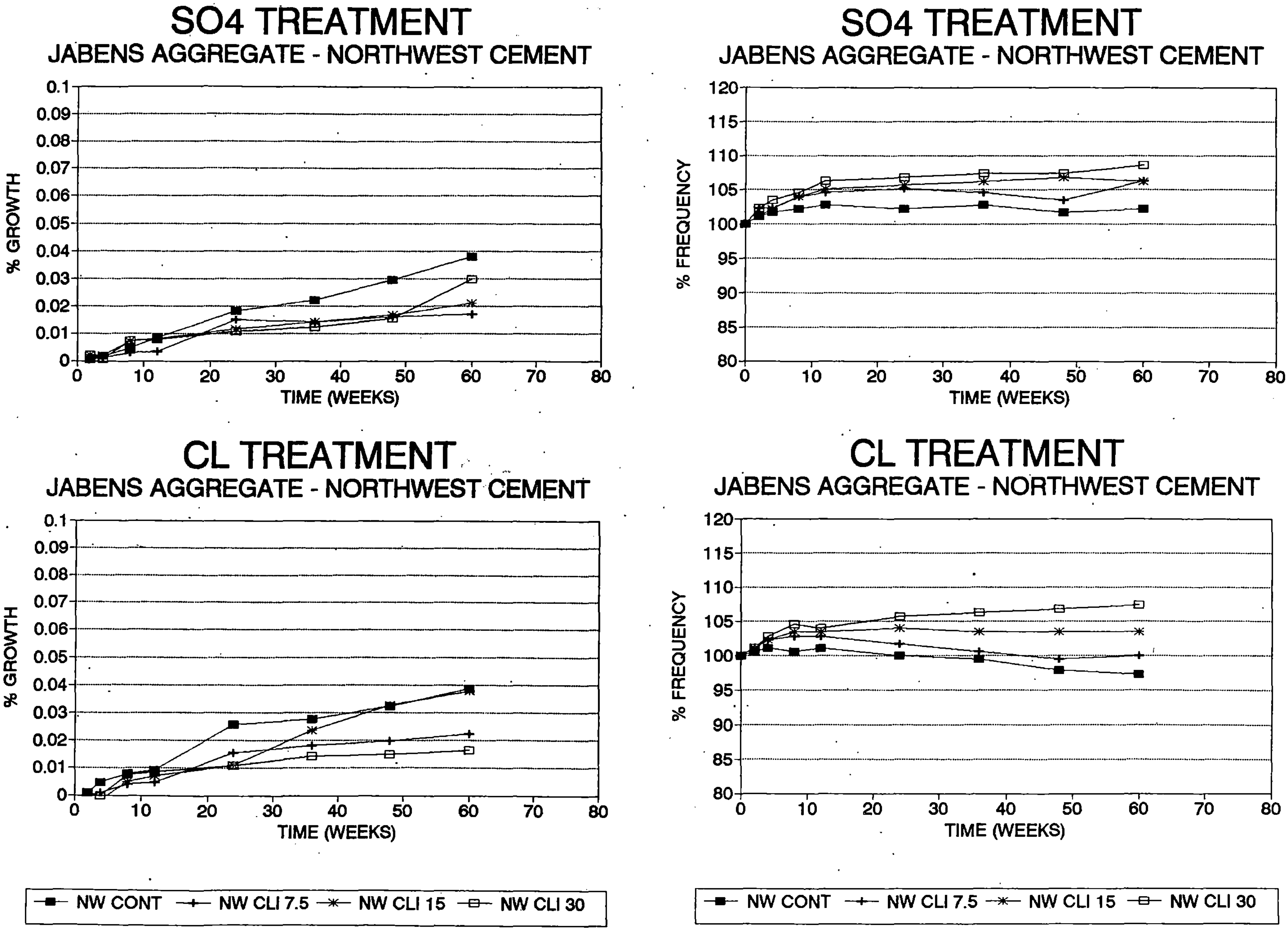


Figure 7, Appendix I. Concrete test results.

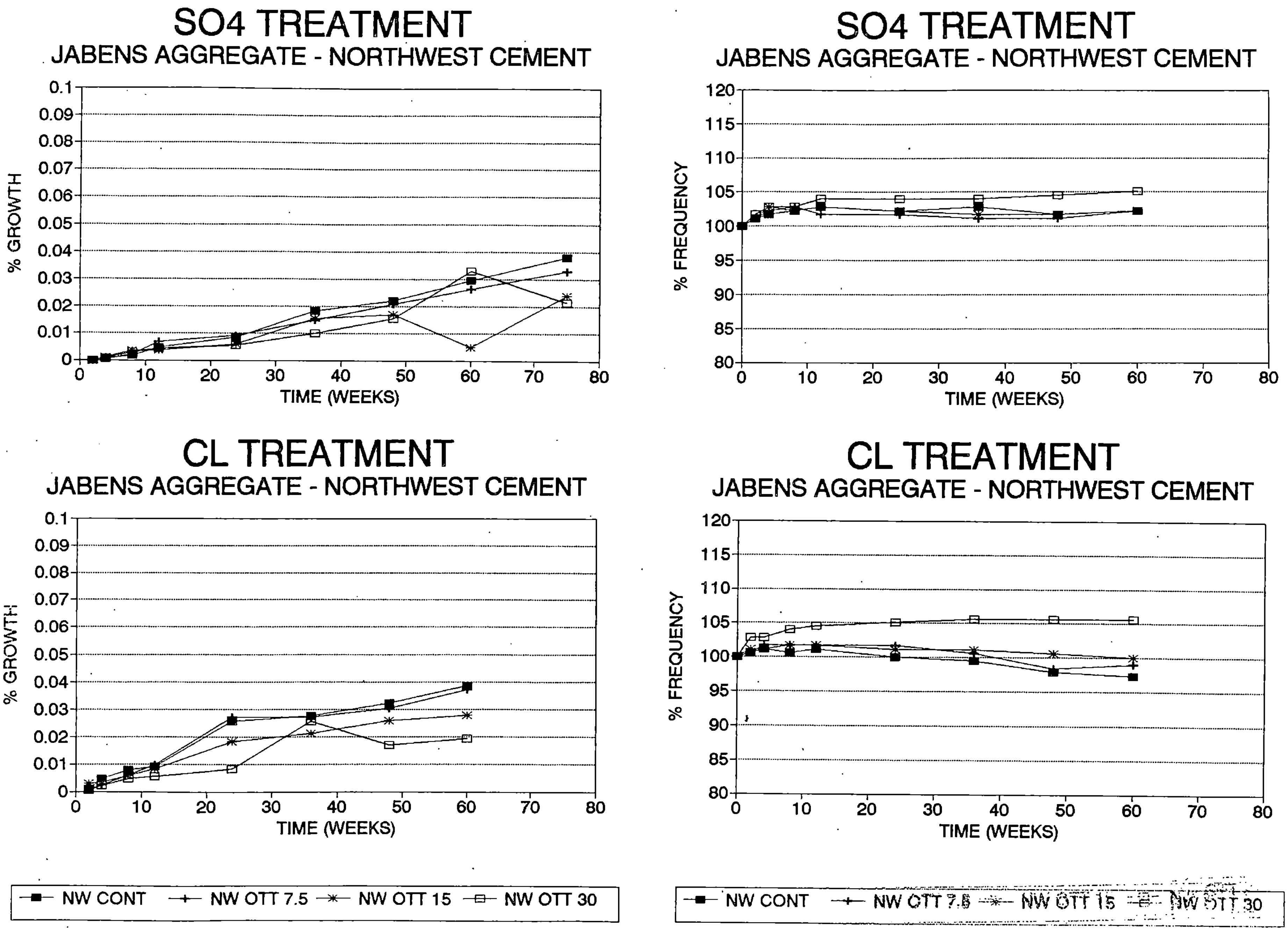


Figure 8, Appendix I. Concrete test results.

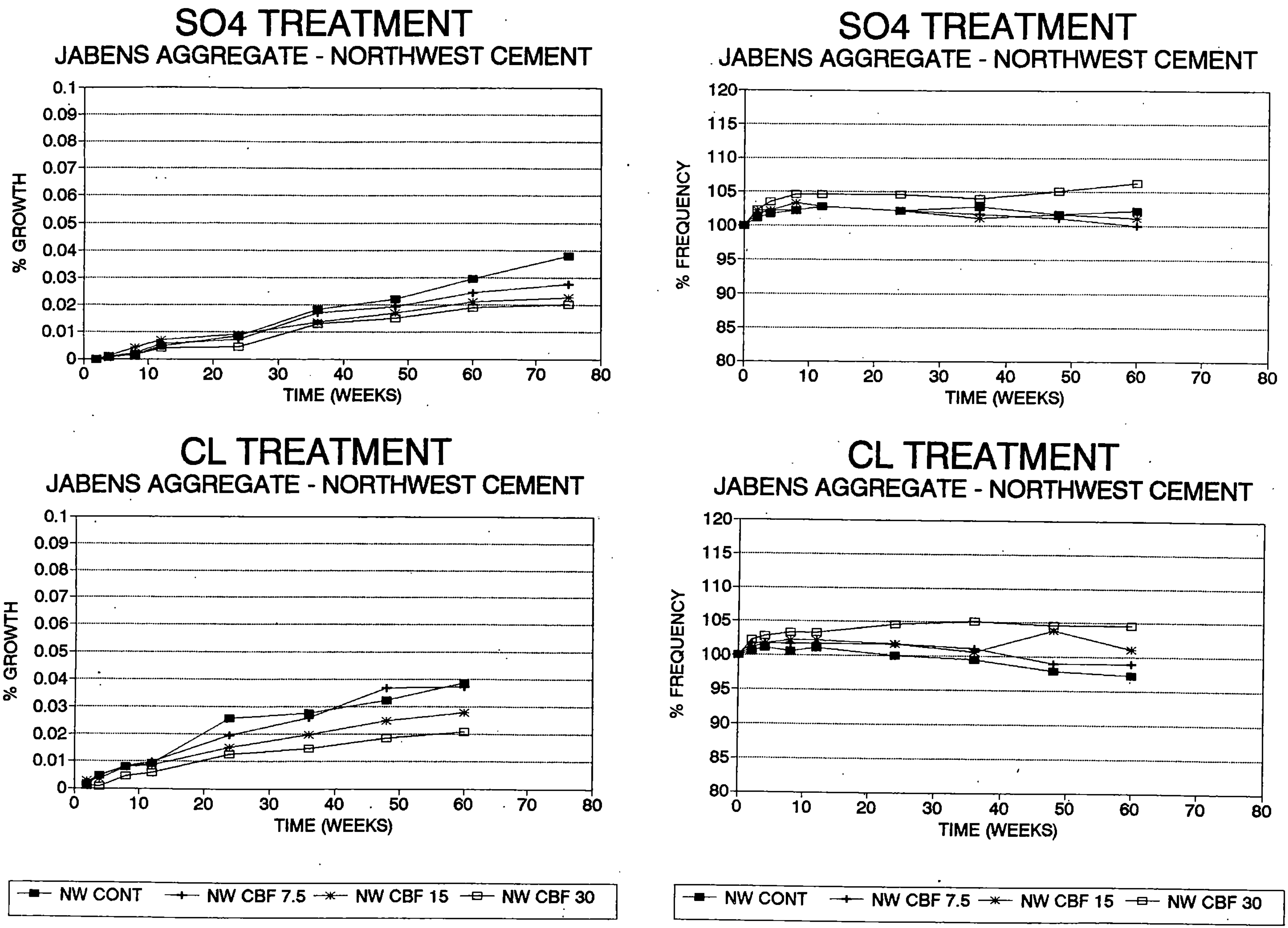


Figure 9, Appendix I. Concrete test results.

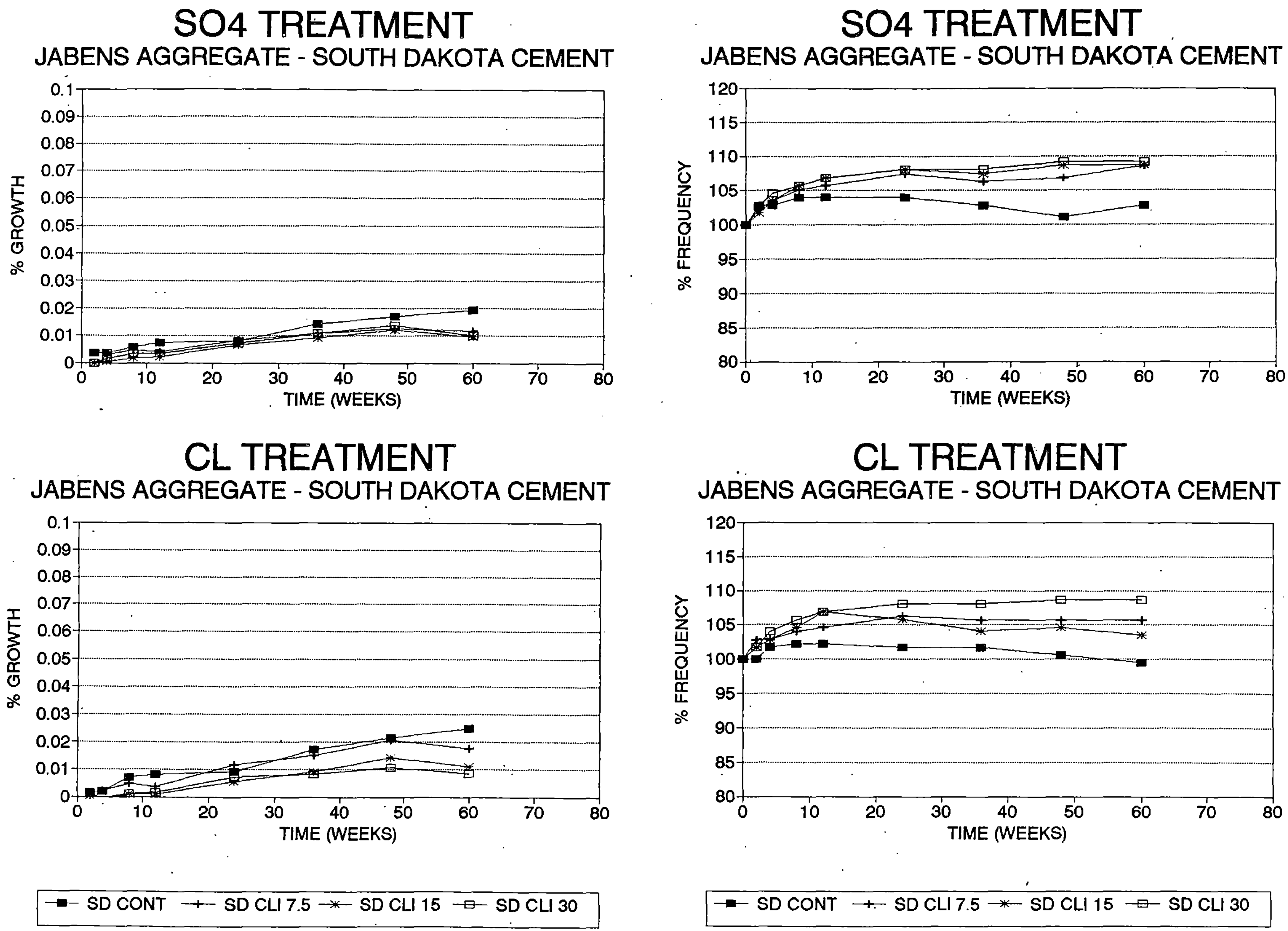


Figure 10, Appendix I. Concrete test results.

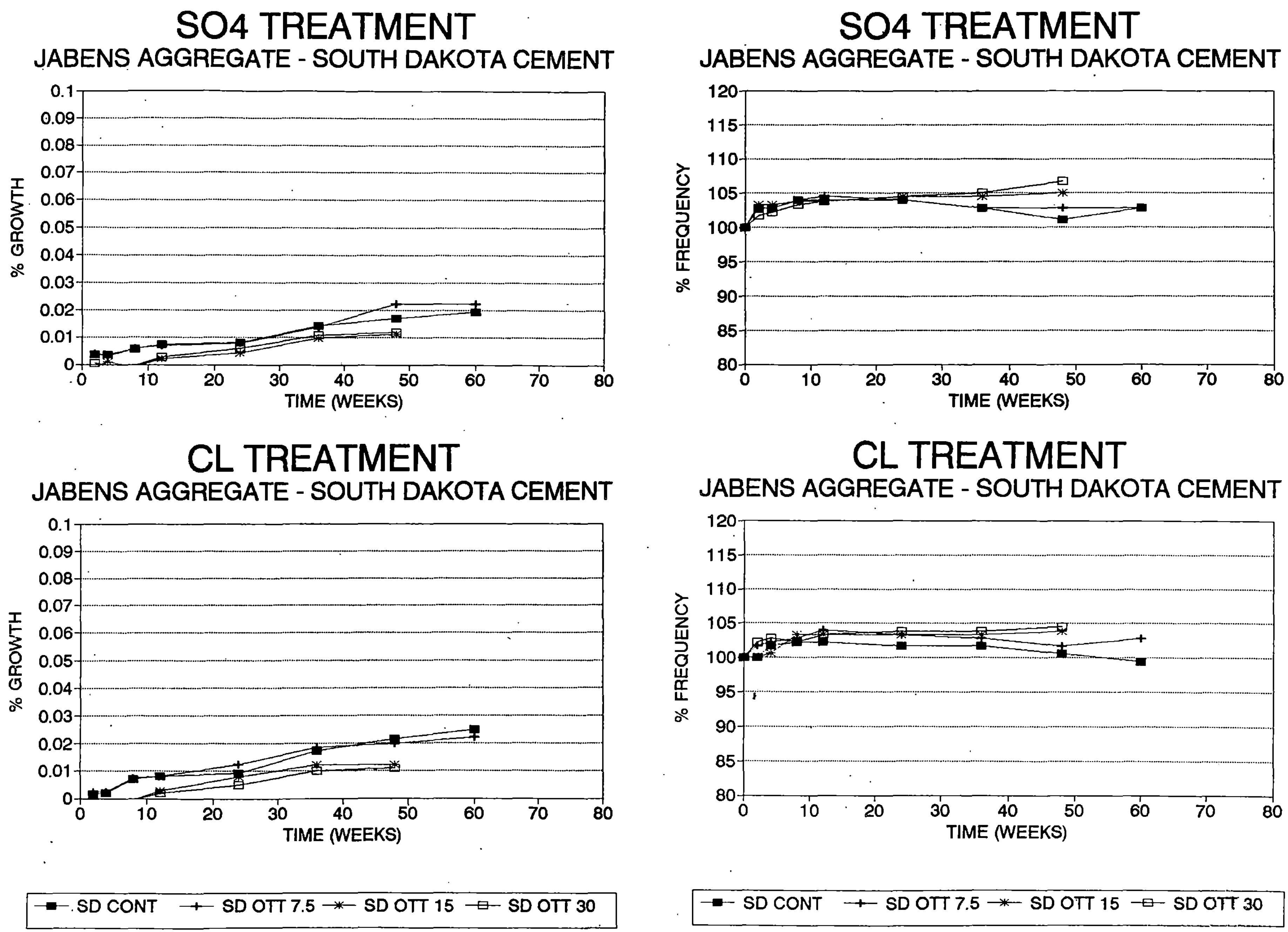


Figure 11, Appendix I. Concrete test results.

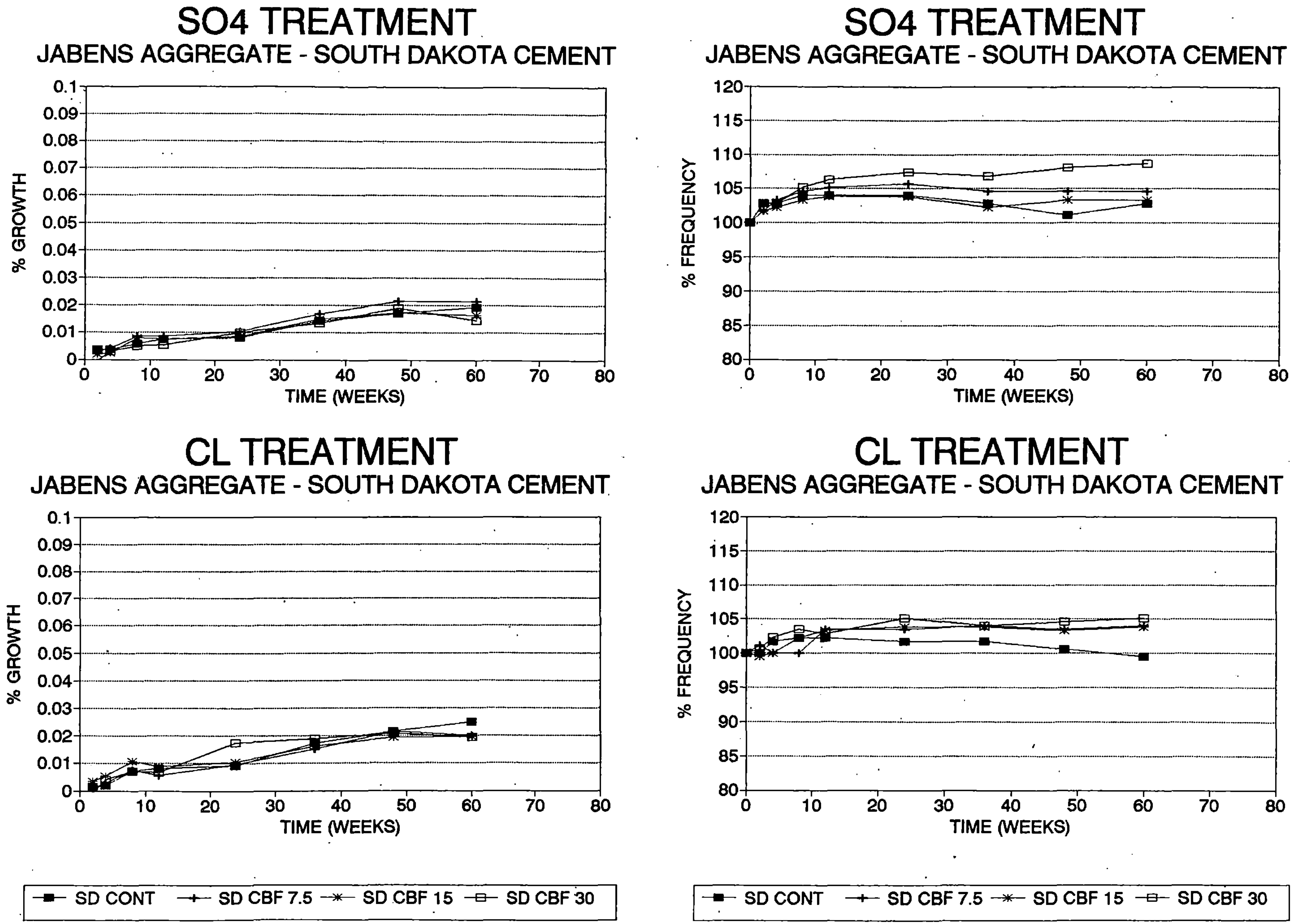


Figure 12, Appendix I. Concrete test results.