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S. Schlorholtz, K.L. Bergeson

Final Report

# Evaluation of the Chemical Durability of Iowa Fly Ash Concretes

March 1993

Sponsored by the Iowa Department of Transportation,  
Highway Division, the  
Iowa Highway Research Board  
and the  
Iowa Fly Ash Affiliate Research Group

Iowa Dot Project HR-327  
ERI Project 3295  
ISU-ERI-Ames 93-411



Iowa Department  
of Transportation



Iowa Fly Ash Affiliate  
Research Group

# report

College of  
Engineering  
Iowa State University

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Civil and Construction Engineering Department

**engineering**  
**research institute**  
iowa state university

"The opinions, findings, and conclusions expressed in this publication are those of the authors and not necessarily those of the Highway Division of the Iowa Department of Transportation, or of the Iowa Fly Ash Affiliate Research Group."

## TABLE OF CONTENTS

ABSTRACT .....	iii
INTRODUCTION.....	1
BACKGROUND AND DEFINITION OF THE PROBLEM.....	1
Sulfate Attack.....	4
Alkali-Aggregate Reactions.....	10
RESEARCH APPROACH.....	17
Sampling Scheme.....	17
Testing Scheme for Sulfate Attack.....	19
Testing Scheme for Alkali Attack.....	21
Chemical Testing Scheme.....	21
RESULTS AND DISCUSSION.....	22
Chemical Tests.....	22
Fly Ashes.....	22
Portland Cements.....	26
Aggregates.....	29
Reagent and Technical Grade Materials.....	29
Abbreviation Summary.....	30
Sulfate Durability Tests - Mortar Bar Specimens.....	31
Curing Study.....	43
Concentration Study.....	46
Sulfate Durability Testing - Paste Study.....	47
Sulfate Durability Tests - Concrete Study.....	51
Alkali Reactivity Tests - Mortar Bar Studies.....	60
SUMMARY AND CONCLUSIONS.....	79
RECOMMENDATIONS.....	83
ACKNOWLEDGMENTS.....	84
REFERENCES.....	85
APPENDIX A (Fly Ash Data)	
APPENDIX B (Cement Data)	
APPENDIX C (Aggregates & Misc. Materials)	
APPENDIX D (Mortar Chemistry)	

## ABSTRACT

The major objective of this research project was to investigate how Iowa fly ashes influenced the chemical durability of portland cement based materials. Chemical durability has become an area of uncertainty because of the winter application of deicer salts (rock salts) that contain a significant amount of sulfate impurities.

The sulfate durability testing program consisted of monitoring portland cement-fly ash paste, mortar and concrete test specimens that had been subjected to aqueous solutions containing various concentrations of salts (both sulfate and chloride). The paste and mortar specimens were monitored for length as a function of time. The concrete test specimens were monitored for length, relative dynamic modulus and mass as a function of time.

The alkali-aggregate reactivity testing program consisted of monitoring the expansion of ASTM C311 mortar bar specimens that contained three different aggregates (Pyrex glass, Oreapolis and standard Ottawa sand).

The results of the sulfate durability study indicated that the paste and concrete test specimens tended to exhibit surface spalling but only very slow expansive tendencies. This suggested that the permeability of the test specimens was controlling the rate of deterioration. Concrete specimens are still being monitored because the majority of the test specimens have expanded less than 0.05 percent; hence, this makes it difficult to estimate the service life of the concrete test specimens or to quantify the performance of the different fly ashes that were used in the study. The results of the mortar bar studies indicated that the chemical composition of the various fly ashes did have an influence on their sulfate resistance. Typically, Clinton and Louisa fly ashes performed the best, followed by the Ottumwa, Neal 4 and then Council Bluffs fly ashes. Council Bluffs fly ash was the only fly ash that consistently reduced the sulfate resistance of the many different mortar specimens that were investigated during this study. None of the trends that were observed in the mortar bar studies have yet become evident in the concrete phase of this project.

The results of the alkali-aggregate study indicated that the Oreapolis aggregate is not very sensitive to alkali attack. Two of the fly ashes, Council bluffs and Ottumwa, tended to increase the expansion of mortar bar specimens that contained the Oreapolis aggregate. However, it was not clear if the additional expansion was due to the alkali content of the fly ash, the periclase content of the fly ash or the cristobalite content of the fly ash, since all three of these factors have been found to influence the test results.

## **INTRODUCTION**

The following report summarizes research activities conducted on Iowa Department of Transportation Project HR-327. The purpose of this research project was to investigate how fly ash influences the chemical durability of portland cement based materials. The goal of this research was 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 was jointly sponsored by the Iowa Department of Transportation (IDOT) and by the Iowa Fly Ash Affiliate Research group. The research work was conducted cooperatively by Iowa State University and Iowa Department of Transportation research personnel. Researchers at Iowa State University conducted the chemical testing and the paste and mortar studies. Researchers at the Iowa Department of Transportation conducted the concrete study.

## **BACKGROUND AND DEFINITION OF THE PROBLEM**

Concrete is a composite material. It consists of a mixture of several different materials that are held together by a binder (normally portland cement). Once the concrete has solidified and hardened, it is commonly regarded as a static building material. However, this is simply not true except in some specific instances. Rather, concrete should be considered a dynamic construction material because its physical and chemical properties change with time, and also with environmental conditions. The "dynamic" idealization of a concrete system is illustrated in Figure 1. Any environmental condition that causes an extreme change in the internal stability (or volume stability) of a hardened concrete structure can lead to severe degradation. The degradation may (or many not) cause a decrease in the service life of the structure. It would be impossible in a single report to describe in detail all of the factors that can influence the durability of concrete materials. Volumes of books have been written on the subject, and our intent is not to delve into the details of the mechanics of slowly deteriorating systems. However, it is important to understand that three major

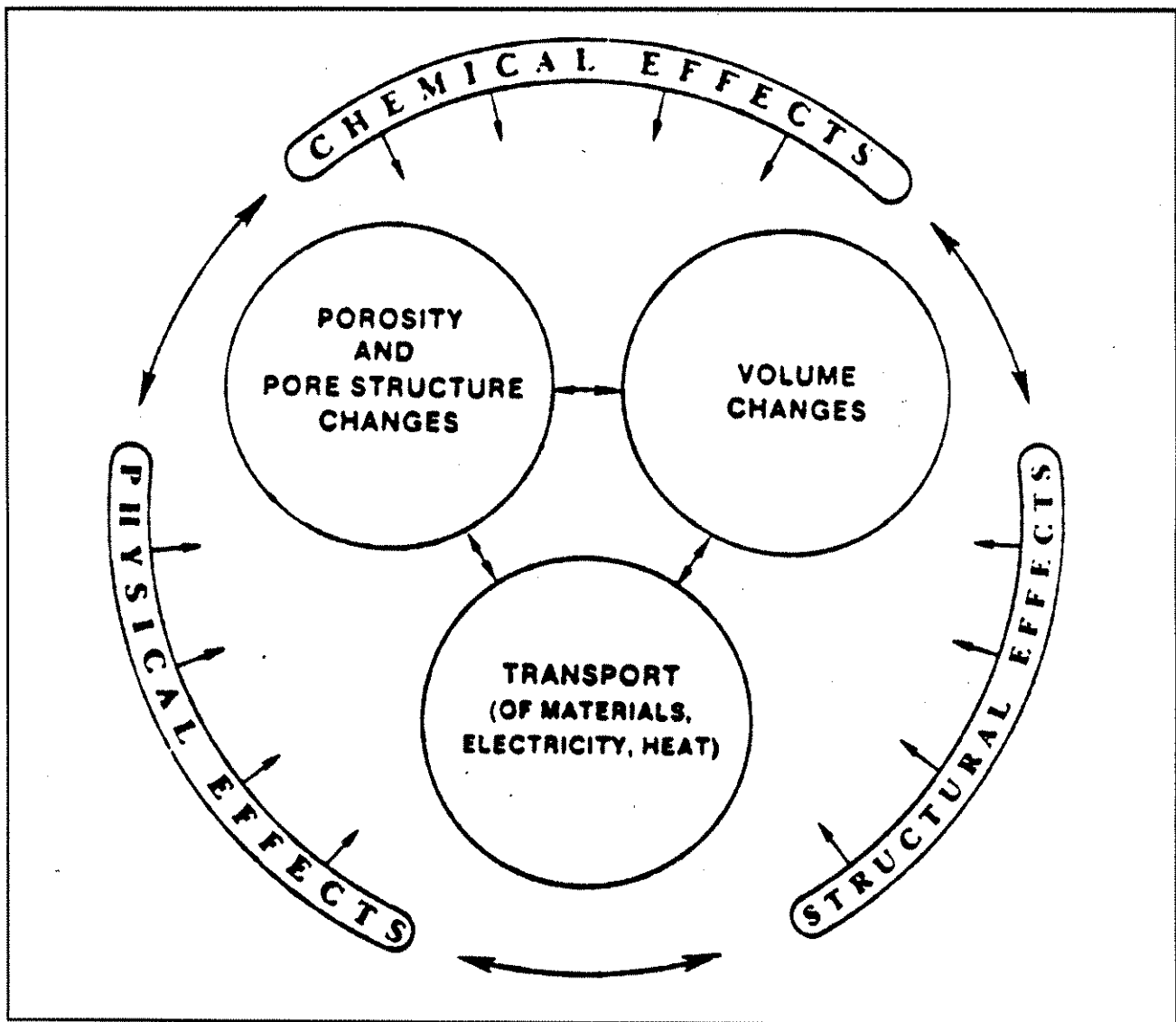


Figure 1. Simplified interrelationships between the environmental effects and internal changes that cause concrete to deteriorate (from reference 1).

items normally control the durability of field concrete. They are as follows.

- materials characteristics
- exposure conditions
- physical and chemical properties of the hardened concrete

Of course, this assumes that the concrete has been properly placed, consolidated and cured, because without proper field construction practices it would be impossible to treat the concrete structure as

isotropic or homogeneous.

The exposure condition of greatest interest to this research project consisted of a simulated deicer salt solution. This was because the rock salt that is commonly placed on Iowa pavements during the winter months consists of a mixture of sodium chloride and calcium sulfate (anhydrite), plus a variety of other minor and/or trace constituents. The concentration of anhydrite in the rock salt is rather small (roughly about 0.5 percent to 6 percent by weight [2] ), and typically the salt meets the requirements for deicing salts that are listed in ASTM D 632 [3]. However, the concentration of anhydrite in the rock salt is definitely large enough to be of concern. Also, it is important to point out that the test method used to determine the NaCl content of the rock salt is rather approximate because it is based on a volumetric test method. The test method, which is based on a titration with a standard silver nitrate solution, is very reliable. However, the test method really only determines the amount of Cl present in the sample; and hence, to express all the Cl as NaCl makes little sense since there may also be KCl,  $\text{CaCl}_2$  or  $\text{MgCl}_2$  present in the sample. This test method should be updated to give a better indication of the elements that are present in the rock salt.

The application of rock salt to a concrete pavement could aggravate two different forms of chemically induced deterioration that are not normally encountered in Iowa, namely sulfate attack and alkali-aggregate reaction. Also, the wide spread use of Class C fly ash in concrete mixes needs to be re-evaluated because some researchers have questioned the performance of similar fly ashes when subjected to sulfate durability testing [4, 5, 6, 7, 8, 9] and alkali-silicate reactivity testing [10, 11, 12]. Many of the test results presented in the various articles have already been summarized and discussed by the authors in a previous report [13], and there is not need to repeat that process here. Instead, the following sections will give only a brief overview of the nature in which sulfates and alkalis attack portland cement based materials. These chemical reactions occur slowly; and hence, researchers have generally adopted accelerated (laboratory) testing methods to estimate field performance. However, be aware that the performance of laboratory specimens often cannot be directly related to field performance. This point has been voiced by many authors but perhaps

R. C. Mielenz has said it best [14]:

"The value of any accelerated test lies in the degree to which the SERVICE CONDITION is simulated and the extent to which the physical, chemical, and mechanical responses of the concrete in the service condition are reproduced in the method of test. Any substantial departure from reality in these respects is likely to produce erroneous decisions in the approval or rejection of the proposed concrete mixture or the treatment that is under investigation.

The need for accelerated tests will be minimized as fundamental research allows quantitative evaluation of those properties that control the response of concrete to its environment."

### **Sulfate Attack**

Portland cement based materials are typically not very durable when subjected to an environment that contains soluble sulfates. In fact, much of the early incentive for creating the different "types" of portland cement was based on the need for solving this recurring durability problem. Today many of the basic questions still remain unanswered. However, for the purpose of this report, we will simply define the two major mechanisms that are commonly attributed to sulfate attack.

The first mechanism is commonly referred to as sulfoaluminate corrosion [15]. In this process the monosulfoaluminate that is present in the hardened concrete product is converted into ettringite by the action of sulfate bearing solutions. This reaction (see Table 1) produces expansion because the solid volume of the product (ettringite) greatly exceeds the solid volume of the reactant (monosulfoaluminate). The expansion eventually leads to cracking and this allows the sulfate bearing solution to penetrate more deeply into the concrete product. Ultimately the concrete disintegrates.

The second sulfate attack mechanism is referred to as gypsum corrosion [15]. In this process calcium hydroxide (a normal by-product of cement hydration) is converted into gypsum by the action of sulfate bearing solutions. This reaction (see Table 1) typically does not produce large expansive pressures. In fact, some researchers question if it produces any expansion at all [16]; however, most field observations indicate that the concrete is substantially "softened" by gypsum



**Table 1. Sulfate attack mechanisms.**

Type of Attack	General Reaction in Aqueous Sulfate Solution
Sulfoaluminate corrosion Cement nomenclature Process	$3\text{CaO}[\text{Al}_2(\text{OH})_6] [\text{CaSO}_4] \cdot 6\text{H}_2\text{O} + 2\text{CaSO}_4 + 19\text{H}_2\text{O} \rightarrow 3\text{CaO}[\text{Al}_2(\text{OH})_6] [3\text{CaSO}_4] \cdot 25\text{H}_2\text{O}$ $\text{C}_4\text{A}\bar{\text{S}}\text{H}_{12} + 2\text{C}\bar{\text{S}} + 18\text{H} \rightarrow \text{C}_6\text{A}\bar{\text{S}}_3\text{H}_{32}$ monosulfoaluminate + sulfate solution $\rightarrow$ ettringite
Gypsum Corrosion Cement nomenclature Process	$\text{Ca}(\text{OH})_2 + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2(\text{OH})^-$ $\text{CH} + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{C}\bar{\text{S}}\text{H}_2 + 2\text{OH}^-$ calcium hydroxide + sulfate solution $\rightarrow$ gypsum + alkali solution

corrosion. Please note in Table 1, that anhydrite ( $\text{CaSO}_4$ ) was used as a reactant in the top set of equations because it is the major comminant present in the rock salts of interest to this research project. The same equations could be written with a variety of different cations (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , etc.) and anions (e.g.,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ , etc.) without a major change in the ultimate response of the concrete structure (i.e., deterioration). However, the rate of deterioration may change significantly depending on the ionic species present in the pore solution of the concrete.

The chemical reactions listed in Table 1 suggest several methods of improving the sulfate resistance of portland cement based materials. First, you can reduce the concentration of monosulfoaluminate present in the concrete. This normally done by reducing the amount of tricalcium aluminate ( $\text{Ca}_3\text{Al}_2\text{O}_6$ ;  $\text{C}_3\text{A}$ ) that is present in the portland cement (i.e., use ASTM Type II and V cements). Tricalcium aluminate is the anhydrous cement mineral which hydrates to produce the ettringite and (ultimately) the monosulfoaluminate that is present in the concrete.

Secondly, you can attempt to stabilize the ettringite phase in the pore solution (i.e., similar to expansive cements). However, excessive amounts of sulfate in the cement can reduce the compressive strength of the concrete and could lead to construction related problems such as false set.

Finally, you can attempt to reduce the amount of calcium hydroxide present in the concrete. This is normally done by incorporating a pozzolan, such as fly ash or silica fume, into the concrete mix design. The pozzolanic reaction consumes calcium hydroxide and produces additional calcium silicate hydrate, this helps to reduce the porosity of the concrete. The major problem with pozzolans is that they are available in a wide variety of different compositions and it is difficult to predict their performance prior to detailed (long-term) laboratory testing [16, 17]. Also, since pozzolans are typically by-products from different industries their composition, and perhaps their sulfate-resistance properties, is sensitive to process related changes in any particular manufacturing plant. However, the benefits gained from the use of reactive pozzolans are typically greatly in excess of those obtained by changing the type of cement used on any given project (see Figure 2).

Other methods can also be used to increase the sulfate-resistance of concrete. Significant gains in sulfate resistance can be made by decreasing the porosity of the concrete mix. This is normally done by lowering the water/cement ratio of the mixture; however, it could also be accomplished by improving the uniformity of the vibration and consolidation of the plastic concrete mix, or by incorporation of a surface treatment that minimizes the penetration of aggressive solutions into the concrete. Figure 3 illustrates the importance of porosity on the predicted life of laboratory concrete pipe specimens subjected to sulfate solutions [17]. In this experiment, the porosity was estimated by using a five hour boiling test and the measured expansion of the test specimens was used to predict the life of any given specimen. It is obvious in Figure 3, that small changes in porosity can drastically influence the durability of the specimens, especially at low porosity values.

One of the major problems that has plagued the study of the sulfate-resistance of portland cement based materials is the lack of standardized test methods. Researchers at different laboratories have adopted different test procedures to better simulate their particular environments. This has been good because it has helped engineers to adapt their concrete mix formulations to a particular set of environmental conditions but it has been bad because it is nearly impossible to compare test results obtained in different parts of the United States (let alone attempting to compare

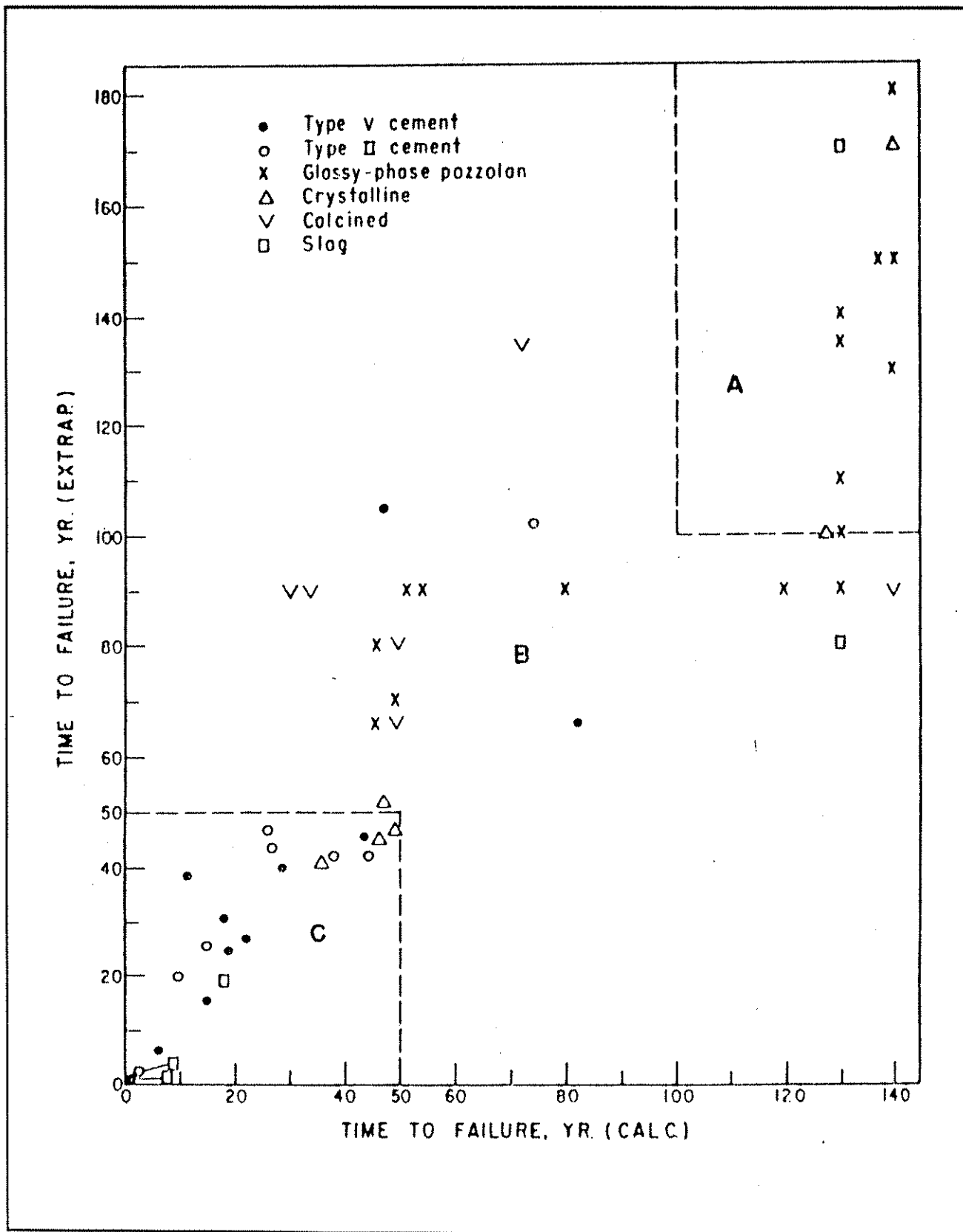
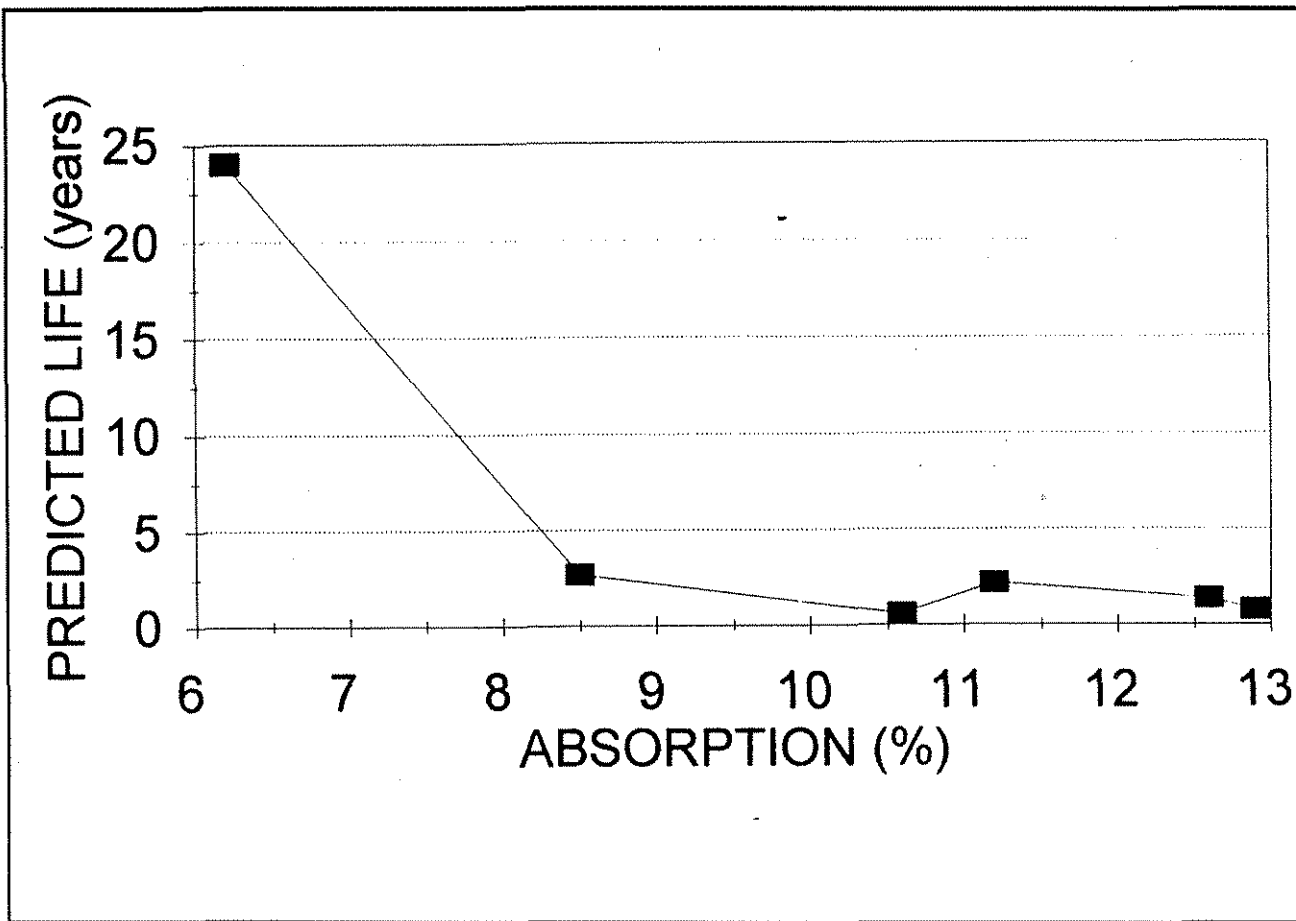


Figure 2. Life expectancies of various concretes in a sodium sulfate environment (from reference 17).



**Figure 3. Predicted life versus specimen absorption for concrete pipe (data from reference 17).**

results from different countries). Hence, little has been done to really probe the fundamental aspects of this recurring durability problem [16].

The most common tests used for estimating the sulfate-resistance of portland cement based materials are summarized in Table 2. In general, the tests are based on soaking test specimens in a sulfate-bearing solution and measuring an appropriate specimen response (such as length change, weight-loss, strength-loss, etc.). However, many different varieties of each test method have been proposed, tested and may currently be in use in different laboratories. Even the ASTM test (C 1012) leaves the test solution unspecified. Hence, Cohen and Mather [16] cut directly to the root of the problem when they suggested that it would be a good time to standardize testing methods before we embark on new sulfate attack studies. After all, how can we accurately predict specimen lifetimes

**Table 2. Test methods for sulfate attack.**

<b>Specimen Type</b>	<b>Dimensions (inches)</b>	<b>Test Method</b>	<b>Measured Response</b>	<b>Solution Type</b>	<b>Comments</b>
Pastes	Varies (typically 1 x 1 x 11.25)	Not specified	Length change Chemistry change Visual rating Mass loss	Varies	Good for research work but practical use is limited because of lack of aggregate interface area.
Mortars	1 x 1 x 11.25	ASTM C 1012	Length change	Varies (suggest 5% sodium sulfate)	Wetting-Drying varieties of this test can be performed. Good chemical testing information can be obtained from the test specimens. Correlation to concrete service life undefined.
Concretes	Varies (from beams to cylinders)	Most methods are similar to Bureau of Reclamation test procedure.	Length change Mass loss Strength loss Visual rating	Varies (typically sodium sulfate from 2 to 10% by wt.)	Wetting-Drying varieties of this test can be performed. Bureau of Reclamation has developed rough correlations to service life.

when we do not even have a consensus on what defines failure?

### **Alkali-Aggregate Reactions**

Some types of concrete aggregates react with the alkaline pore solution in concrete to produce a gel-like material. This gel-like material has the potential to swell; and hence, produce cracks that can disrupt the integrity of the concrete. Such behavior is commonly referred to as an alkali-aggregate reaction (AAR). Alkali-aggregate reactions are normally classified into three different categories: {1} alkali-silica reactions; {2} alkali-silicate reactions; and {3} alkali-carbonate reactions. However, as with any complex natural process, the different AAR categories may act independently or in unison with the other processes that cause concrete to deteriorate prematurely (i.e., freeze-thaw attack, sulfate attack, etc.).

Much research has been conducted to investigate both the fundamental and practical aspects of AAR. In fact, a recent literature review [18] gives an excellent overview of the literature pertaining to alkali-silica (and silicate) reactions. The number of published papers that discuss AAR has been increasing substantially over the past two decades (see Figure 4). This can be attributed to a heightening awareness of concrete durability problems. The awareness has, in part, been generated by the scientific community because of international conferences on AAR (held in 1975, 1976, 1978, 1981, 1983, 1987 and 1989 - these correspond roughly to the "spikes" in the number of publications shown in Figure 4). However, research is often driven by the observation of poor field performance. Poor field performance of concrete can be attributed to recent changes in cement manufacturing processes (i.e., dry process kilns tend to increase alkali content), depletion of high-quality (proven service record) aggregate reserves and the routine application of deicer salts (typically NaCl). Also, recent investigations have indicated that nearly all siliceous aggregates are to some degree alkali-sensitive; however, the reactivity may be so slow that it may not significantly influence the design life of the concrete product [19].

Alkali-carbonate reactivity (ACR) is normally used to describe the reaction of alkalis (Na and K, typically from the cement) with dolomite crystals in fine-grained calcitic dolomites and

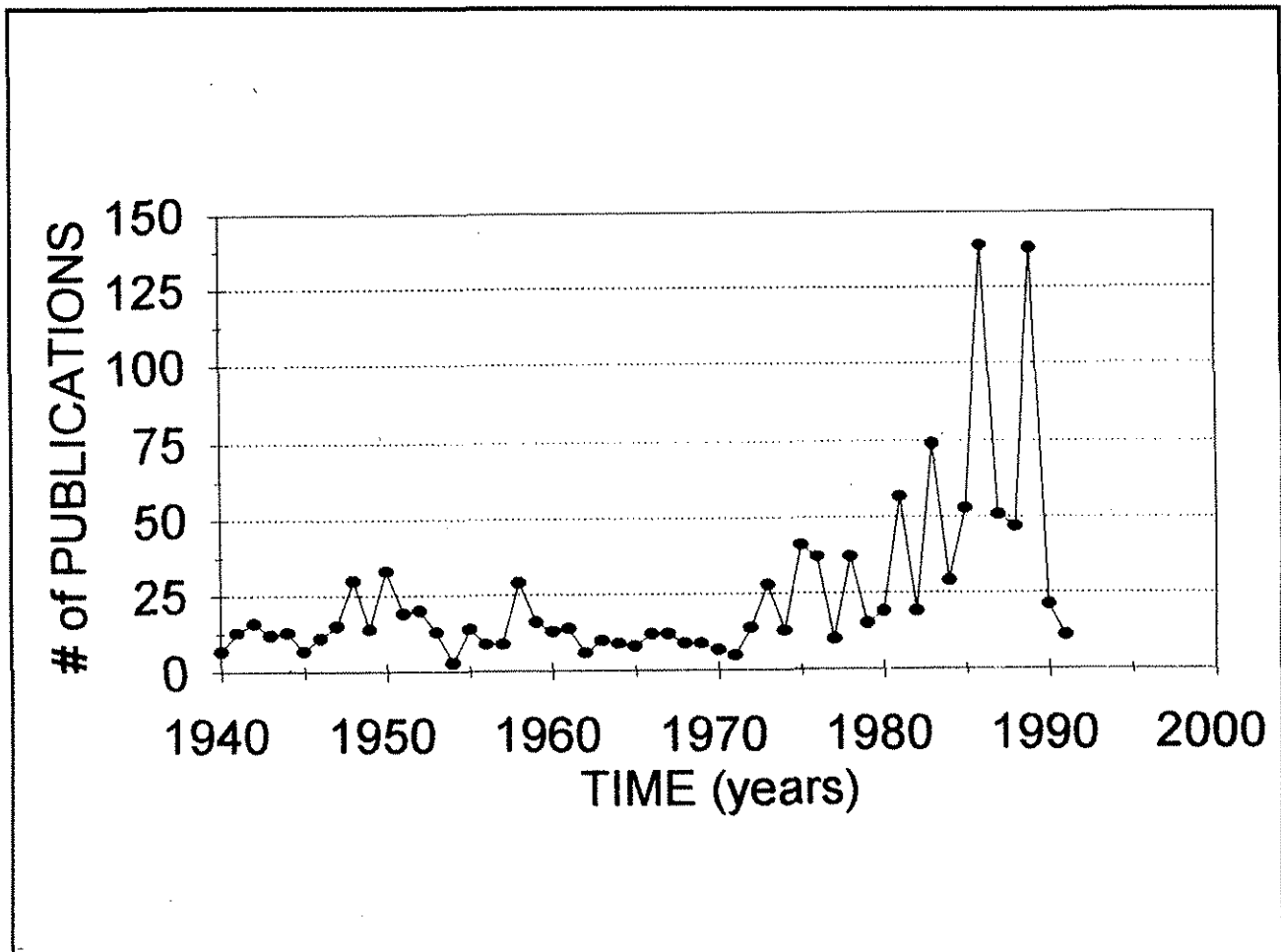
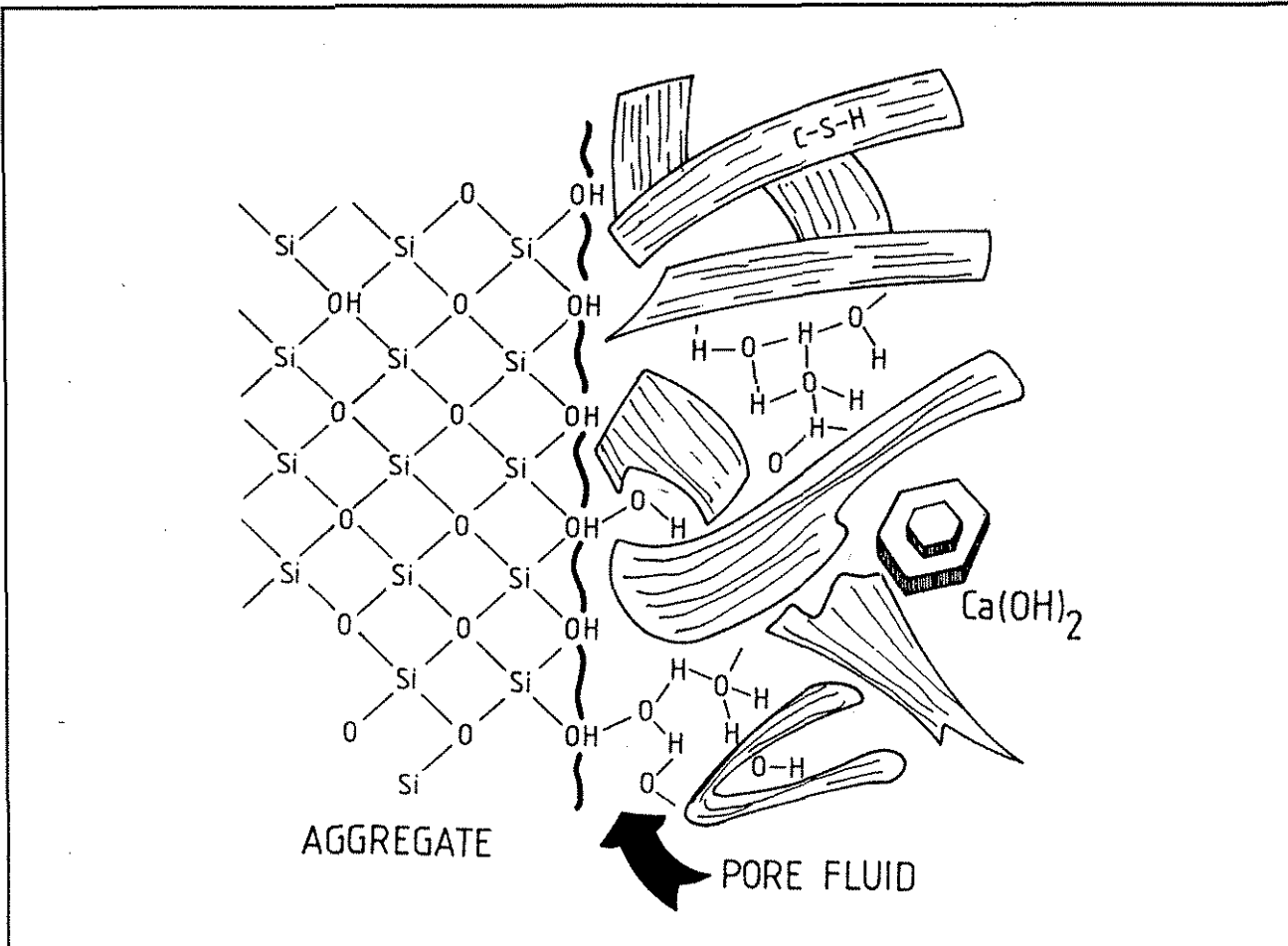


Figure 4. Number of publications concerning alkali-silica reactivity vs. time (data from reference 18).

dolomitic limestones [12, 20]. The exact mechanism of this reaction is not fully understood. Hence, ACR will not be discussed in detail in this report.

Alkali-silica and alkali-silicate reactions are often discussed together because they are fundamentally quite similar. The difference between the two categories of attack is based simply on the fact that alkali-silica attack refers to the reaction of alkalis with the polymorphs of silica (i.e., chemical formula  $\text{SiO}_2$ , such as quartz, tridymite, cristobalite, etc.), while alkali-silicate attack refers to the various silicate minerals that may decompose in the presence of a strongly alkaline pore solution (i.e., feldspars, argillites, etc.). The alkali-silica reaction (ASR) is probably the most commonly observed form of AAR [19].

The mechanism of ASR can briefly be summarized as follows [21, 22, 23]. First, consider the concrete system shown in Figure 5. The concrete system that is shown has been greatly magnified to illustrate on a microscopic scale, the various constituents that are commonly present.



**Figure 5. A magnified view of a typical concrete system (from reference 22).**

These consist of {1} aggregate (infinitely large in this instance, note how the surface has been hydrated; {2} cement hydration products (calcium hydroxide, calcium silicate hydrate plus some unreacted cement grains); and {3} pore solution (mostly water). A very simplistic set of chemical reactions for ASR are listed in Table 3. ASR tends to occur when mass transfer across the aggregate-pore solution boundary is constricted [21, 22], this leads to a buildup of alkali silica gel at the interface. The alkali-silica gel is unstable relative to its surroundings and may swell



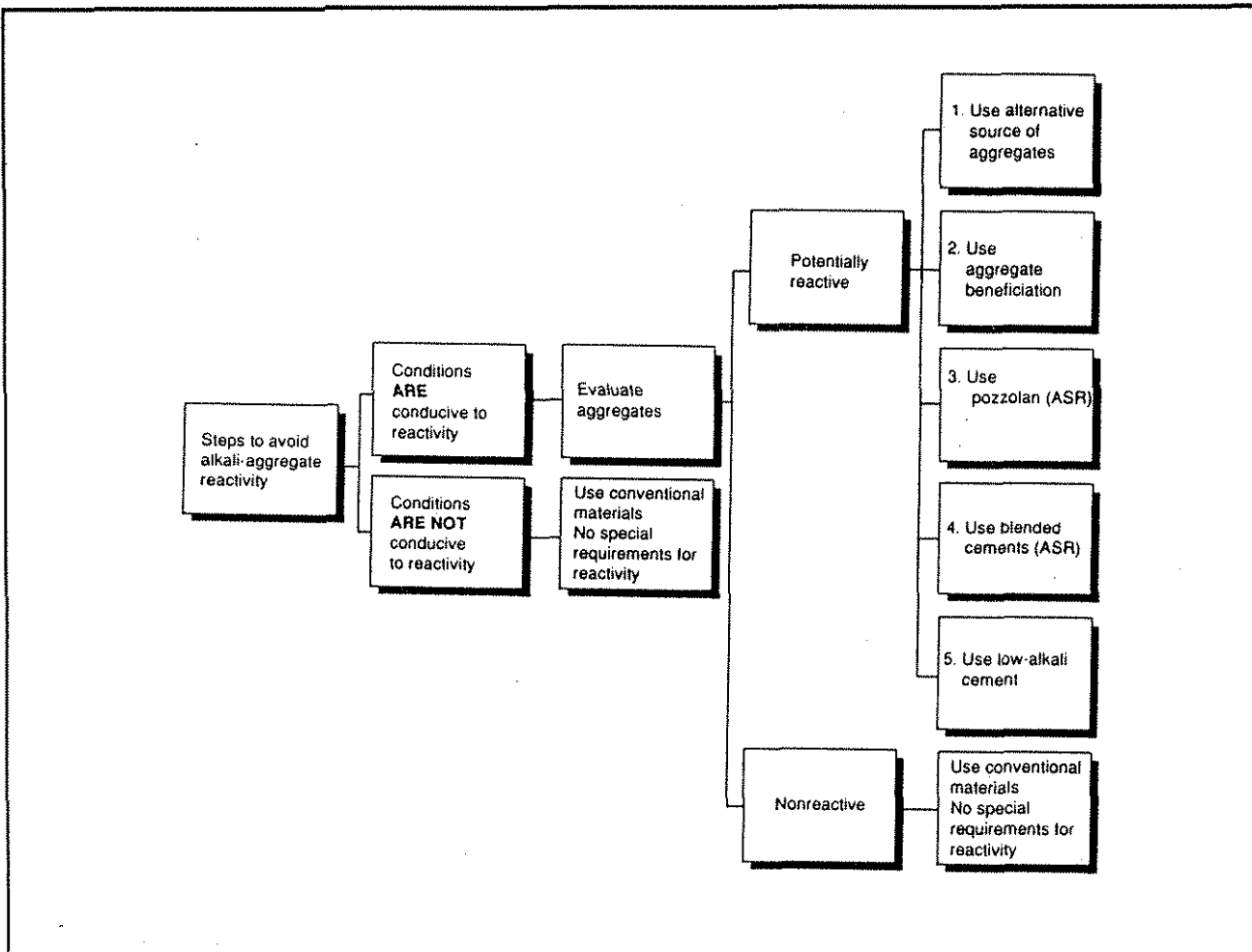
**Table 3. Alkali-silica reaction mechanisms.**

Mechanism	Simplified Reactions (from reference 21)
Acid-base neutralization	$\text{-- Si -- OH} + \text{NaOH} \rightarrow \text{-- Si -- O}^-\text{Na}^+ + \text{H}_2\text{O}$ $\text{hydrated surface of particle} + \text{alkalis} \rightarrow \text{gel} + \text{water}$
Siloxane attack	$\text{-- Si -- O -- Si --} + 2\text{NaOH} \rightarrow \text{-- Si -- O}^-\text{Na}^+ + \text{Na}^+\text{O}^-\text{-- Si --} + \text{H}_2\text{O}$ $\text{siloxane bridge} + \text{alkalis} \rightarrow \text{gel} + \text{water}$

through imbibition or it may be further altered by the pore solution (mostly  $\text{Ca}^{2+}$  exchange). The imbibition of water by the gel is highly variable and appears to depend on both the composition and the rigidity of the gel. Expansion (swelling) pressures exceeding 600 psi have been reported in the literature [24, 25]. Obviously, pressures (tensile stresses) of this magnitude can cause deformation and subsequent cracking of the concrete product.

There are many strategies that can be employed to minimize AAR. A recent flow chart published by the Portland Cement Association [12] is reproduced in Figure 6. This chart is useful because it defines a practical thought process that can be used by engineers to specify better concrete mixes. For instance, if a concrete mix is to be designed for a humid environment and it incorporates an alkali-reactive aggregate, then the flow chart immediately suggests a series of options that can be used to minimize the potential AAR problem. However, the diagram fails to mention some of the technical difficulties that are commonly encountered when attempting to distinguish "reactive" aggregates from "non-reactive" aggregates, or "reactive" mineral admixtures from "non-reactive" mineral admixtures. Such distinctions are normally made on the basis of accelerated laboratory tests (i.e., screening studies) and/or field service records. Hence, materials testing again plays a central role in defining "reactivity."

A summary of the different test methods that are available for measuring the AAR potential of concrete aggregates is given in Table 4. Modifications of these different test methods are also commonly used to assess the effectiveness of different mineral admixtures/cement combinations in



**Figure 6. Flow chart that can be used to minimize AAR problems (from reference 12).**

mitigating the effect of AAR. Table 4 was adapted from reference 26 (only slight modifications) to indicate the wide variety of test methods that have evolved during the study of the AAR problem (i.e., since about 1940!). No attempt will be made to outline the details, assumptions or deficiencies of the various test methods. Interested readers should consult the original source [26] for such details. The types of tests listed in Table 4 have been denoted as fundamental (F) or secondary (S).

The fundamental tests are normally conducted on the individual aggregate sources to assess their innate reactivity. This may consist of identifying a reactive constituent through petrographic work or may consist of reacting an aggregate with a strongly alkaline solution to see if it dissolves or expands. Hence, these tests can be conducted quite rapidly.

**Table 4. Test methods for alkali-aggregate reactivity.**

Type	Test Method	Approximate Time Required
F	Petrographic Investigation ASTM C 295	days for detailed work
F	ASTM C 586 (Rock Cylinder Method for alkali carbonate reactivity)	at least 1 month
F	Chemical Test Methods ASTM C 289 Modified ASTM C 289 (run on acid-insoluble residue) German Dissolution Test Osmotic Cell Test Gel Pat Test Chemical Shrinkage Method	2 or 3 days 2 or 3 days 1 day less than 40 days about 1 week 1 day
S	Mortar Bar Methods ASTM C 227 and C 441, same 1 AFNOR P 18-585 Method CCA Method Danish Accelerated Method NBRI or ASTM C 9-Proposal-P214 Autoclave methods (Chinese, Japanese, Canadian)	at least 6 months 6 months 6 months 5 months at least 2 weeks about 3 days
S	Concrete Prism Methods CAN/CSA A23.2-14A Method AFNOR P 18-587 Method South Africa Method BSI 812 Method CCA Method Accelerated Method (used in Quebec) Autoclave Methods ASTM C 1105 (alkali carbonate reactivity)	1 year 8 months about 3 weeks 1 year 6 months 1 month a few days at least 3 months

Secondary tests employ mixtures of portland cement and other materials. Normally only a single variable is monitored, namely expansion. Hence, these tests depend both on the materials characteristics (i.e., alkali content of the cement, reactivity of the pozzolan, gradation of the aggregate, etc.) and the experimental procedure that is employed (i.e., types of containers used to store specimens, type of accelerating medium such as temperature, pressure or concentration, etc.). Attempts are often made to correlate specimen performance (expansion) to field service performance

and/or the fundamental testing methods. This is generally done because the secondary tests may take several months (or even a year in some instances) to complete.

Mineral admixtures, such as pozzolans or slags, are often used to improve the performance of concretes that contain alkali-sensitive aggregates. The beneficial effects of pozzolans are difficult to pinpoint; however, they are often attributed to the fact that {1} they tend to release alkalis to the pore solution much slower than portland cements (i.e., low soluble alkali content); and {2} they contain a considerable amount of reactive silica and alumina that can react with the pore solution to create more calcium silicate hydrates (i.e., the pozzolanic reaction). For these two reasons concretes containing pozzolans tend to have pore solutions with lower hydroxyl ion concentrations and mortar fractions with lower permeabilities than conventional portland cement concretes. Obviously, both hydroxyl ion concentration and permeability play significant roles in AAR.

Taylor [23] has noted similarities between the pozzolanic reaction and the chemistry that is normally associated with ASR. In fact, he has proposed that they are both essentially the same chemical reaction but that the local environment dictates the expansivity of the mixture. His reasoning is as follows [23].

"In the pozzolanic reaction, the alkali silicate gel is formed in an environment rich in  $\text{Ca}^{2+}$  and, except in a narrow zone close to the reacting surface, is quickly converted into C-S-H. In ASR, it is formed in an environment that is poor in  $\text{Ca}^{2+}$ , and massive outflows of gel may result. The cement paste cannot supply  $\text{Ca}^{2+}$  fast enough to prevent much of this gel from persisting for periods. This situation is especially marked if the alkali silicate gel forms within the aggregate particles, as is the case with opal."

This also helps to explain why even the most alkali-sensitive aggregates tend to behave as pozzolans when they are ground into fine powders. It also helps to explain why both aggregates and pozzolans tend to exhibit "pessimum" type behavior when they are used in portland cement mortars or concretes.

The "pessimum" effect is illustrated in Figure 7. Plots of linear expansion versus reactive component concentration (either aggregate or pozzolan) often exhibit this behavior because the expansion process can be controlled by the alkali content of the pore solution or the reactive silica

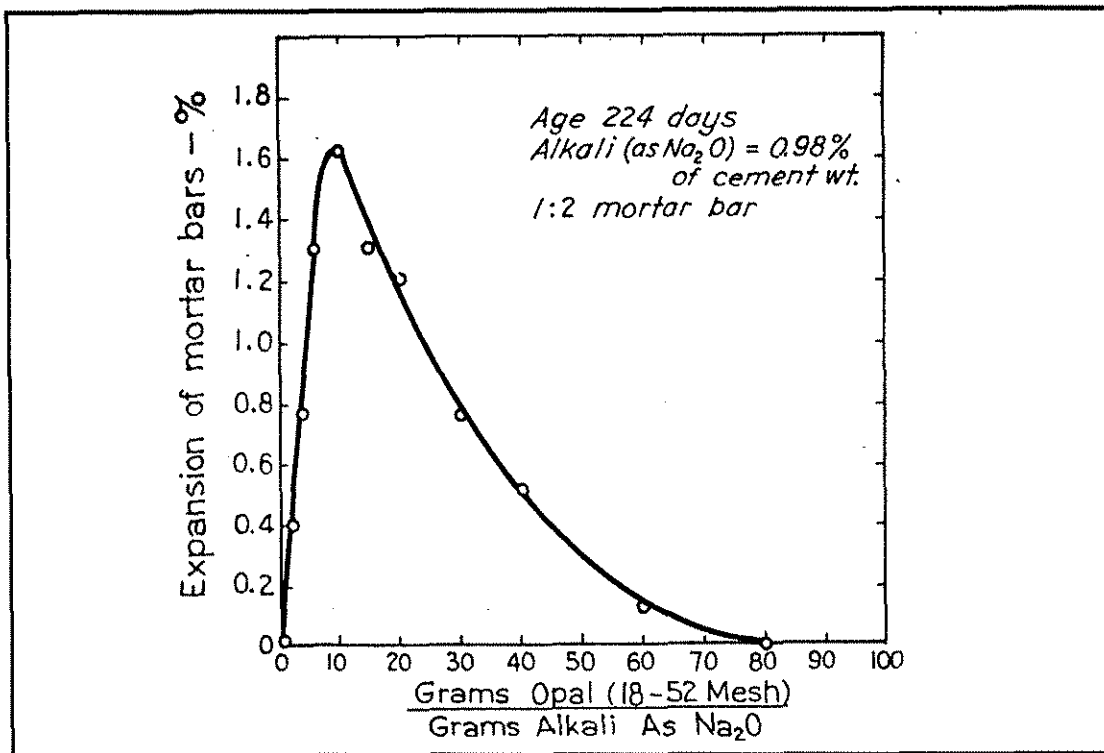


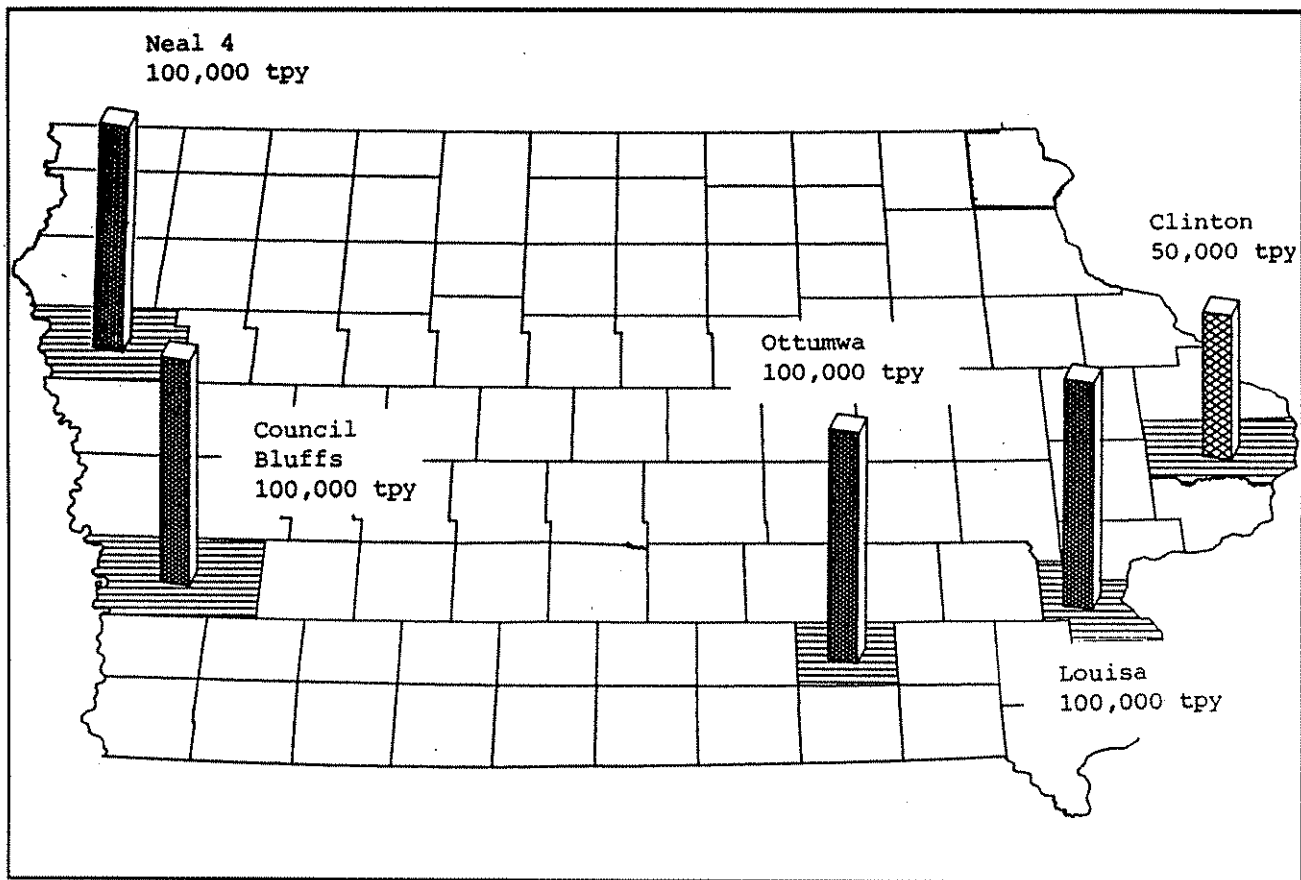
Figure 7. An illustration of pessimum effect in laboratory test specimens (from reference 21).

concentration of the mixture. If the aggregate (or pozzolan) is very reactive then it quickly removes all the alkali from the pore solution and expansion decreases with increasing aggregate content because of a dilution effect. Note, that the pessimum conditions apply to a closed system. The introduction of alkalis to the system via an external source (i.e., deicer salts, etc.) drastically complicate the pessimum effect.

## RESEARCH APPROACH

### Sampling Scheme

Fly ashes from Council Bluffs (unit #3), Louisa, Port Neal (unit #4) and Ottumwa generating stations were selected to represent the range of Class C fly ashes available in Iowa. Fly ash from M.L. Kapp generating station (Clinton) was selected to represent the Class F fly ashes available in Iowa. The general locations and ash production rates of the various power plants are illustrated in Figure 8. Details concerning the various power plants are summarized in Appendix A.



**Figure 8. General location and amount of fly ash produced at power plants studied in this project.**  
(tpy = tons per year)

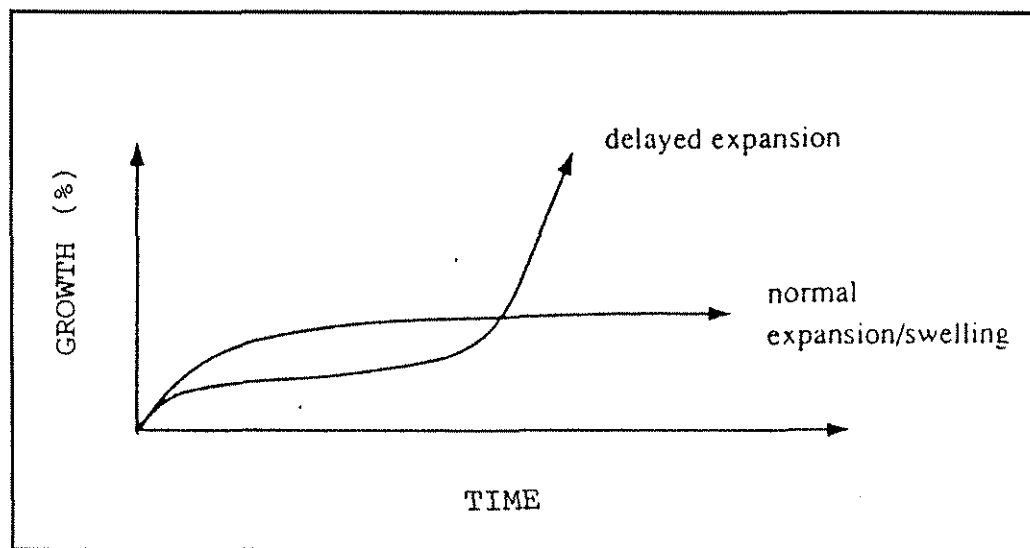
The fly ash sample from a given power plant was taken on a single day (i.e., the samples were not composite samples). Enough sample was taken from each power plant to approximately fill two 55 gallon drums (i.e., roughly 500 pounds of fly ash). The fly ash samples were then delivered to the Materials Analysis and Research Laboratory (MARL) at Iowa State University where they were sub-sampled, labeled and dated. The MARL personnel then delivered one barrel of each source of fly ash to the Iowa Department of Transportation (Iowa DOT) Materials Laboratory for use in the concrete portion of the research project.

Three different sources of portland cement were chosen for use in the project. Two of the sources produced Type I portland cement, while the remaining source produced Type V (sulfate resistant) portland cement.

The Type I portland cements consisted of a low alkali cement (Dundee) from Mason City, Iowa, and a moderate alkali cement from Davenport, Iowa. The Type V cement was obtained from Rapid City, South Dakota. All of the cements were delivered to the laboratory in standard (94 lb) bags.

### **Testing Scheme for Sulfate Attack**

Many different criteria can be used to estimate the sulfate resistance of portland cement products. For this research project specimen growth (or linear expansion) was the major property that was used to evaluate the durability of portland cement-fly ash pastes, mortars and concretes immersed in sulfate bearing solutions. Concrete specimens were also monitored for weight change and dynamic modulus of elasticity (sonic modulus). The typical response that was expected from any given specimen is illustrated in Figure 9. Failure can be defined as some predetermined value of growth or the experiment can be continued until the specimen physically disintegrates.



**Figure 9. Diagram illustrating the response of test specimens to sulfate attack.**  
(adopted from reference 16).

Concrete specimens for sulfate durability testing were prepared at the Iowa DOT. The concrete mixes employed two sources of cement (Type I and Type V), four sources of fly ash

(Council Bluffs, Louisa, Ottumwa, and Clinton), and four different coarse aggregates (Jabens, Lamont, Montour, and Early Chapel). The fine aggregate used for the mixes was from near Bellevue, Iowa. All of the concrete mixes were proportioned using Iowa DOT C-3 mix specifications. Fly ash was replaced for cement on a 1 to 1 weight basis throughout this study. Water/cement ratio was adjusted to meet the slump criterion for C-3 mixes. Fly ash replacements of 7.5, 15 and 30 percent (by weight) were used in this study. Concrete beams with nominal dimensions of 4" x 4" x 18" were molded for sulfate durability testing. Two cylinders (4.5" x 9") were also molded from the mix to evaluate the 28 day compressive strength of the concrete. All of the beam specimens were moist cured for at least 28 days before immersion in the sulfate solution.

Aqueous solutions with two different concentrations of sulfate were used in the concrete study. The first solution contained 10 percent  $\text{Na}_2\text{SO}_4$  (by weight), this solution has been used by other researchers [9], and has proven to be quite aggressive to portland cement concretes. The second solution contained 10 percent mixed salt (by weight). The composition of the mixed salt was 95 percent NaCl and 5 percent  $\text{Na}_2\text{SO}_4$ , this was used to simulate a "worse case" deicing salt. Hence, the second solution ultimately contained 9.5 percent NaCl and 0.5 percent  $\text{Na}_2\text{SO}_4$ . Technical grade (or better) purity  $\text{Na}_2\text{SO}_4$  and NaCl were used to make both solutions.

Mortar specimens for sulfate durability testing were prepared in accordance with ASTM C 1012 [3], with two notable exceptions. First, the accelerated curing method described in ASTM C 1012 was not used. Instead, specimens were demolded after one day of moist curing and then placed in saturated lime water until they reached a minimum strength of 2850 psi. The strength versus time relationship was established using two inch cube specimens that were molded, cured and tested as described in ASTM C 109 [3]. Secondly, only two specimens (rather than the four suggested by the ASTM) were molded for each mixture. 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 subjected to aqueous solutions containing two different concentrations of sulfate. The first solution contained 5 percent  $\text{Na}_2\text{SO}_4$  (by weight). The second solution contained 9.5 percent NaCl and 0.25 percent  $\text{Na}_2\text{SO}_4$  (by weight). Reagent grade NaCl and



Na<sub>2</sub>SO<sub>4</sub> were used in the mortar phase of this study. A tank containing lime water was used to assess the expansive potential of many of the mortar mixes.

Paste specimens for sulfate durability testing were mixed using a procedure developed in our earlier studies [27]. Since paste specimens are homogenous on a small scale, a preliminary experiment was performed to see if small cylindrical test specimens (13/16" diameter by 3" long) could be substituted for the larger (1" x 1" x 11.25") prismatic specimens. Only one concentration of sulfate solution (5 percent Na<sub>2</sub>SO<sub>4</sub>) was used to assess durability of the paste specimens.

The preliminary results of the small cylindrical specimens indicated that there were severe experimental constraints involved when using the small specimens. Hence, the experiment was repeated using 1" x 1" x 11.25" prismatic specimens. The paste mixtures were composed of one type of cement (Dundee), two different fly ashes (Council Bluffs and Clinton), and replacement levels of 15 percent and 30 percent (by weight) of fly ash for cement. A water/cement of 0.35 was used in the study. All of the specimens were exposed to a 5 percent solution of sodium sulfate.

### **Testing Scheme for Alkali Attack**

Mortar specimens for alkali attack were made in accordance with ASTM C 311[3], except that only two specimens were prepared from each mix rather than the three specimens dictated by the specification. This study used two Type I portland cements, all five of the fly ash samples mentioned earlier in this report, and three different fine aggregates (pyrex glass, standard ASTM C 109 sand, and a Class V aggregate from Oreapolis, Iowa). Five different levels of fly ash replacement (7.5, 15, 22.5, 30 and 50 percent) were used in this research project.

### **Chemical Testing Scheme**

All of the raw materials were subjected to chemical tests. Typically, x-ray analysis was used to define both the bulk composition and the minerals present in a given material.

X-ray diffraction (XRD) was used to identify the major and minor crystalline constituents present in each material. A Siemens D 500 x-ray diffractometer was used throughout this study.

The diffractometer was controlled by a PDP 11/23 computer via an LC500 interface. A copper x-ray tube was used for all diffraction work. The diffractometer was equipped with a diffracted beam monochromator and medium resolution slits.

X-ray fluorescence (XRF) analysis was used to quantify the major, minor, and selected trace elements in the various materials. A Siemens SRS 200 sequential x-ray spectrometer was used for all of the analyses. The spectrometer was fully computer controlled. A chrome x-ray tube was used throughout the study.

A Beckman DU-2 flame photometer was used to determine the available alkali content (Na and K expressed as equivalent  $\text{Na}_2\text{O}$ ) of the various fly ashes. An oxygen-hydrogen flame was used for all analyses.

Thermogravimetric analysis (TG or TGA) was performed on selected mortar specimens. A TA Instrument (previously known as DUPONT) 2000 thermal analysis system was used throughout this study. The system utilizes a TA Hi-Res. TGA module equipped with a 16 sample carousel. A typical experiment used the following experimental parameters: {1} a scanning rate of  $40^\circ$  per minute, resolution = 5; {2} a sample mass of about 10 milligrams; {3} a dynamic nitrogen atmosphere purged at 100 ml per minute; and {4} test specimens were heated from ambient (about  $25^\circ\text{C}$ ) to  $970^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Chemical Tests

#### Fly Ashes

The chemical compositions of the five fly ash samples used in this project are listed in Table 5. The fly ashes were also subjected to a physical testing program similar to that suggested in ASTM C 618. The results of the physical testing program are listed in Appendix A. Overall, the five fly ashes chosen for the research program exhibited a good range of chemical and physical properties.

The five fly ashes were also subjected to x-ray diffraction analysis. The compounds identified in the various diffractograms are summarized in Table 6. Please note that some of the compounds listed in Table 6 are not directly evident in the diffractograms of the bulk fly ashes;

**Table 5. Summary of bulk chemistry of the fly ash samples.**

Oxide (Wgt %)	Sample				
	Clinton	Louisa	Ottumwa	Neal 4	Council Bluffs
SiO <sub>2</sub>	51.1	35.9	30.9	35.1	30.8
Al <sub>2</sub> O <sub>3</sub>	18.4	22.8	20.2	18.0	16.9
Fe <sub>2</sub> O <sub>3</sub> (T)	14.1	5.8	5.9	5.7	6.9
Sum:	83.6	64.5	57.0	58.8	54.6
SO <sub>3</sub>	1.8	1.5	2.7	3.2	4.0
CaO	5.0	23.2	26.3	26.6	29.1
MgO	1.2	4.4	4.8	4.9	6.5
P <sub>2</sub> O <sub>5</sub>	0.15	1.46	2.12	1.14	0.63
K <sub>2</sub> O	2.06	0.51	0.35	0.39	0.24
Na <sub>2</sub> O	0.9	1.4	2.1	1.3	1.9
TiO <sub>2</sub>	0.95	1.55	1.42	1.41	1.28
SrO	0.03	0.39	0.47	0.41	0.42
BaO	0.07	0.78	0.97	0.83	0.75
Moisture Content	0.12	0.01	0.05	0.08	0.05
Loss on Ignition	1.05	0.14	0.23	0.41	0.26
Available Alkali	0.91	1.28	2.08	0.95	1.68
Repeat:	0.91	-	1.81	0.94	1.62
% Acid Soluble	12.7	69.6	75.8	70.3	74.4
ASTM Class	F	C	C	C	C
Tricalcium Aluminate (C <sub>3</sub> A, wgt %)	ND not detected	4.5	6.5	6.0	7.7

however, additional treatments (i.e., acid extraction, particle size separation, heat treatment, etc.) were used to verify the presence of the various compounds. The various diffractograms are located in Appendix A.

Currently it is not possible to accurately estimate the amounts of the various compounds present in the fly ashes. However, due to the influence of tricalcium aluminate on sulfate attack, the amount of tricalcium aluminate present in each fly ash was estimated using quantitative x-ray

**Table 6. Compounds identified in the five fly ash samples.**

Compound	Clinton	Louisa	Ottumwa	Neal 4	Council Bluffs
Quartz, low (SiO <sub>2</sub> , JCPDS #33-1161)	M	M	M	M	M
Anhydrite (CaSO <sub>4</sub> , JCPDS #6-226)	m	M	M	M	M
Periclase (MgO, JCPDS #4-829)	-	m	m	m	M
Lime (CaO, JCPDS #4-777)	m	T	m	m	m
Ferrite Spinel [(Mg, Fe) (Fe, Al) <sub>2</sub> O <sub>4</sub> ]	M	m	m	m	m
Mullite (Al <sub>6</sub> Si <sub>2</sub> O <sub>13</sub> , JCPDS #15-776)	M	m	m	m	m
Tricalcium Aluminate (Ca <sub>3</sub> Al <sub>2</sub> O <sub>6</sub> , JCPDS #38-1429)	-	M	M	M	M
Hematite (Fe <sub>2</sub> O <sub>3</sub> , JCPDS #33-664)	?	T	T	T	T
Tetracalcium Trialuminate Sulfate (JCPDS #33-256)	-	-	m	-	m
Cristobalite (SiO <sub>2</sub> , JCPDS #11-695)	-	-	m	m	m

**M = Major component****m = minor component****T = trace component****? = question**

diffraction. The tricalcium aluminate estimate was made by spiking the raw fly ash samples with known amounts of pure tricalcium aluminate (cubic structure, XRD pattern matched JCPDS#38-1429). Note in Table 5, that all of the fly ash samples had tricalcium aluminate contents of less than 8 percent (by weight).

All of the diffractograms indicated that a large amount of a given fly ash was amorphous to x-rays (i.e., glassy). Each of the Class C fly ashes exhibited a glass scattering halo that reached a maximum intensity at about 30 degrees 2-theta (Cu K $\alpha$  radiation). The Class F fly ash (Clinton) exhibited a glass scattering halo that reached a maximum intensity at about 23 degrees 2-theta. This indicated that the Class C fly ashes contained a different type of glass than the Class F fly ash.

To obtain additional information about the glass phases and minor components present in the five fly ash samples, the raw fly ashes were digested in hot acid (HCl) using a procedure described in an earlier Iowa DOT report [27]. The acid insoluble residue was then subjected to x-ray analysis. Also, the acid insoluble residue was ignited at 950° C to recrystallize the glass portion of the residue. The minerals identified in this phase of the study have already been summarized in Table 6. X-ray diffractograms of the various treatments can be found in Appendix A. However, there are a couple of findings that must be emphasized. First, the acid insoluble residue from all five fly ashes contained very similar mineral assemblages. Even the glass portion of the fly ashes appeared to be similar. And secondly, the recrystallization process had little influence on the glass present in the Clinton and the Louisa samples, but it caused cristobalite to crystallize from the remaining fly ashes (Neal 4, Ottumwa and Council Bluffs). This was important because cristobalite is an alkali-sensitive material and it has the potential to influence the ASR tests that will be discussed later in this report.

The results of XRF analysis on the acid insoluble fraction of the five fly ash samples are listed in Table 7. In general, the XRF results were in excellent agreement with the XRD results. The acid insoluble residue is primarily composed of siliceous material.

A study was conducted to assess the amount of alkalis (Na and K) that could be leached from the various samples of raw fly ash. This study should be applicable to the alkali durability portion of this research project. Briefly, the available alkali test procedure (see ASTM C 311 [3]) was used to extract and measure the amount of alkalis (expressed as equivalent  $\text{Na}_2\text{O}$ ) that were leached in to the solution after various curing times. The results of this study are illustrated in Figure 10. Note that the dissolution rate of fly ash alkalis was quite rapid for the first 14 to 28 days, then it decreased significantly. However, as is apparent in Figure 10, a considerable amount of alkalis were still being released into solution after 28 days of curing. Also, the Louisa and Neal 4 fly ashes, which have relatively low available alkali values at 28 days, either exceed or approach the ASTM C 618 available alkali specification limit (maximum = 1.50 percent equivalent  $\text{Na}_2\text{O}$ ) after longer curing times. Figure 10 indicates that it takes about 60 days to reach the plateau in the alkali dissolution curves for the Class C ashes and about 30 days for the Class F ash. These test results for the Class C

**Table 7. Summary of acid insoluble fraction of the fly ash samples.**

Oxide (Wgt %)	Sample				
	Clinton	Louisa	Ottumwa	Neal 4	Council Bluffs
SiO <sub>2</sub>	56.0	62.6	61.3	70.5	68.7
Al <sub>2</sub> O <sub>3</sub>	19.2	18.1	13.0	10.2	9.0
Fe <sub>2</sub> O <sub>3</sub> (T)	15.5	5.7	7.5	5.8	7.0
Sum:	90.7	86.3	81.8	86.5	84.7
SO <sub>3</sub>	0.0	0.3	0.9	0.5	0.7
CaO	0.7	3.9	4.9	4.4	4.7
MgO	0.9	1.3	1.4	1.4	1.8
P <sub>2</sub> O <sub>5</sub>	0.06	0.20	0.30	0.11	0.08
K <sub>2</sub> O	2.03	0.66	0.48	0.66	0.41
Na <sub>2</sub> O	0.2	0.8	1.9	1.5	2.2
TiO <sub>2</sub>	0.98	1.42	1.43	1.28	1.31
SrO	0.02	0.13	0.22	0.13	0.15
BaO	0.07	1.07	2.40	1.39	1.85
Loss on Ignition	0.98	1.75	1.89	1.92	1.21

ashes are in conflict with earlier studies at this laboratory [28], that indicated that all of the alkalis should eventually be released to the pore solution. We are still trying to resolve this conflicting information.

### **Portland Cements**

The portland cements used in this study have been subjected to a series of physical and chemical tests. The cement tests were conducted in accordance with the ASTM methods specified for portland cements [29].

The chemical compositions of the three cements are summarized in Table 8. These assays were obtained by using the XRF techniques discussed earlier in this report. The amount of cement minerals present in each source of cement were calculated using the Bogue equations listed in ASTM C 150 [29]. Note that the Davenport cement had a chemical composition similar to a Type II

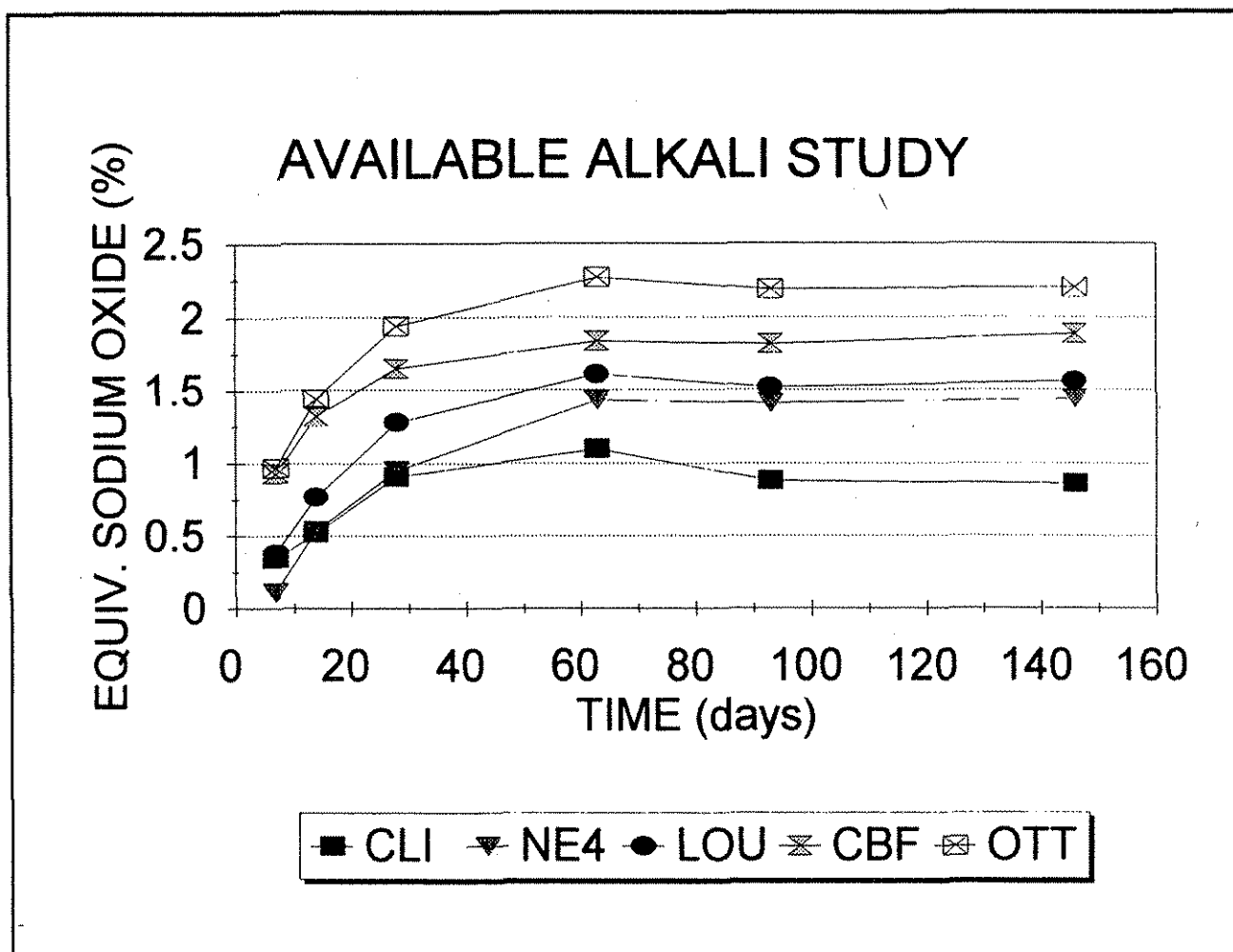


Figure 10. Available alkali content versus time for the five fly ashes used in this study.

cement; however, its  $C_3S + C_3A$  content was slightly high which placed it in the Type I portland cement category. The Davenport cement will be referred to as Type I-II cement throughout the rest of this report.

X-ray diffractograms of the three cements are located in Appendix B. The results of the XRD tests were in good agreement with the XRF assays. The major compounds identified in the cements were alite (substituted tricalcium silicate; subst.  $-C_3S$ ), belite (substituted dicalcium silicate; subst.  $-C_2S$ ), a mineral close to tetracalcium aluminoferrite ( $C_4AF$ ) and tricalcium aluminate ( $C_3A$ ). Various sulfate bearing minerals were identified as minor constituents in the three cements. The

**Table 8. Chemical and physical characteristics of the portland cements.**

Chemical Properties		Sample		
Oxide (wgt %)	South Dakota	Dundee	Davenport	
SiO <sub>2</sub>	22.57	21.27	21.03	
Al <sub>2</sub> O <sub>3</sub>	3.53	4.70	4.23	
Fe <sub>2</sub> O <sub>3</sub>	3.43	1.93	2.80	
CaO	64.6	64.4	63.0	
MgO	1.06	2.11	3.43	
SO <sub>3</sub>	1.94	3.08	2.63	
Loss on Ignition	1.07	1.16	1.04	
Na <sub>2</sub> O	0.11	0.10	0.16	
K <sub>2</sub> O	0.36	0.44	0.91	
TiO <sub>2</sub>	0.16	0.17	0.24	
P <sub>2</sub> O <sub>5</sub>	0.08	0.01	0.12	
SrO	0.13	0.03	0.06	
Calculated Cement Compounds (wgt %)	South Dakota	Dundee	Davenport	
C <sub>3</sub> S	55.7	56.2	54.3	
C <sub>2</sub> S	22.7	18.6	19.3	
C <sub>3</sub> A	4.2	9.7	7.4	
C <sub>4</sub> AF	10.4	5.9	8.5	
Cement Type	V	I	I (close to II)	
Equivalent Alkali (% Na <sub>2</sub> O)	0.35	0.39	0.76	
Physical Properties	South Dakota	Dundee	Davenport	
Normal Consistency (%)	24.8*	25.0*	24.8*	
Compressive Strength (psi) @ 1 day	1820	2120	1980	
@ 2 days	2940	3090	2780	
@ 3 days	3640	3660	3110	
Blaine Fineness (m <sup>2</sup> /Kg)	378*	403*	386*	
Vicat Initial Set Time	OK*	OK*	OK*	

\* = value from Iowa DOT test report



Davenport cement contained bassanite, anhydrite and perhaps some gypsum; while the remaining two cements contained only gypsum and bassanite.

The physical properties of the three cements, namely normal consistency, compressive strength (C 109 mortar cubes), fineness and set time are listed in the lower portion of Table 8.

### **Aggregates**

X-ray diffractograms of the Jabens, Lamont, Montour and Early Chapel aggregates (crushed stone for the concrete mixes) are located in Appendix C. The minerals identified in the diffractograms are listed in Table 9. The results of XRF analysis are summarized in Table 10.

The results of XRD and XRF analysis of the fine aggregates that were used in the alkali reactivity study are listed in Tables 9 and 10, respectively. Diffractograms of the various fine aggregates are located in Appendix C.

**Table 9. Results of XRD analysis of the aggregate samples.**

Mineral	Coarse Aggregates				Fine Aggregates	
	Jabens	Lamont	Montour	Early Chapel	Oreapolis Class V	Ottawa Sand C 109
Calcite ( $\text{CaCO}_3$ )	m	T	M	M	-	-
Dolomite ( $\text{MgCa}(\text{CO}_3)_2$ )	M	M	T	m	-	-
Quartz ( $\text{SiO}_2$ )	T	T	T	m	M	M
Feldspar	-	-	-	-	m	-
Pyrite	-	-	T	-	-	-

**M = Major phase**

**m = minor phase**

**T = trace evident**

### **Reagent and Technical Grade Materials**

The x-ray diffractograms of the sodium chloride, sodium sulfate and rock salt used during this project are located in Appendix C. The major compounds identified in the various diffractograms correspond to the desired material (i.e., sodium chloride or sodium sulfate); however, the rock salt did contain a significant amount of anhydrite ( $\text{CaSO}_4$ ). The results of XRF analysis are summarized in Table 11. In general, the technical grade materials compared very well with the

**Table 10. Results of XRF analysis of the aggregate samples.**

Oxide (Wgt %)	Jabens	Lamont	Montour	Early Chapel	Pyrex Glass*	Oreapolis Class V	C109 Sand
SiO <sub>2</sub>	1.61	1.82	0.27	2.77	85.1	81.7	98.5
Al <sub>2</sub> O <sub>3</sub>	0.21	0.20	0.05	0.40	3.0	10.2	0.1
Fe <sub>2</sub> O <sub>3</sub>	0.65	0.22	0.60	0.60	0.2	1.1	0.7
CaO	35.2	30.5	53.1	52.4	0.02	0.5	0.1
MgO	14.7	20.9	0.41	0.71	N/M	1.1	0.1
SO <sub>3</sub>	0.38	0.02	0.20	0.04	< 0.1	< 0.1	< 0.1
K <sub>2</sub> O	0.08	0.07	0.01	0.08	0.02	3.2	< 0.01
TiO <sub>2</sub>	0.02	0.02	< 0.01	0.02	N/M	N/M	N/M
P <sub>2</sub> O <sub>5</sub>	0.02	< 0.01	< 0.01	0.02	N/M	N/M	N/M
SrO	0.02	0.02	0.02	0.04	N/M	N/M	N/M
MnO	0.04	0.01	0.02	0.04	N/M	N/M	N/M
Na <sub>2</sub> O	N/M	N/M	N/M	N/M	4.9	2.1	< 0.1
Loss on Ignition	44.5	46.0	42.4	42.4	0.3	0.25	0.04

N/M = not measured

\* = average composition of two lots of Pyrex glass

reagent grade materials. The rock salt contained about 3 percent anhydrite plus a few other minor elements.

### **Abbreviation Summary**

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

DUN = Dundee cement = Type I  
 DAV = Davenport cement = Type I-II  
 SDV = South Dakota cement = Type V  
 CLI = Clinton fly ash (Class F)  
 LOU = Louisa fly ash (Class C)  
 OTT = Ottumwa fly ash (Class C)  
 NE4 = Neal 4 fly ash (Class C)  
 CBF = Council Bluffs fly ash (Class C)  
 CON = Control Mortar = control

**Table 11. Results of XRF analysis on reagent and technical grade chemicals.**  
(all values in parts per million (ppm) unless noted otherwise)

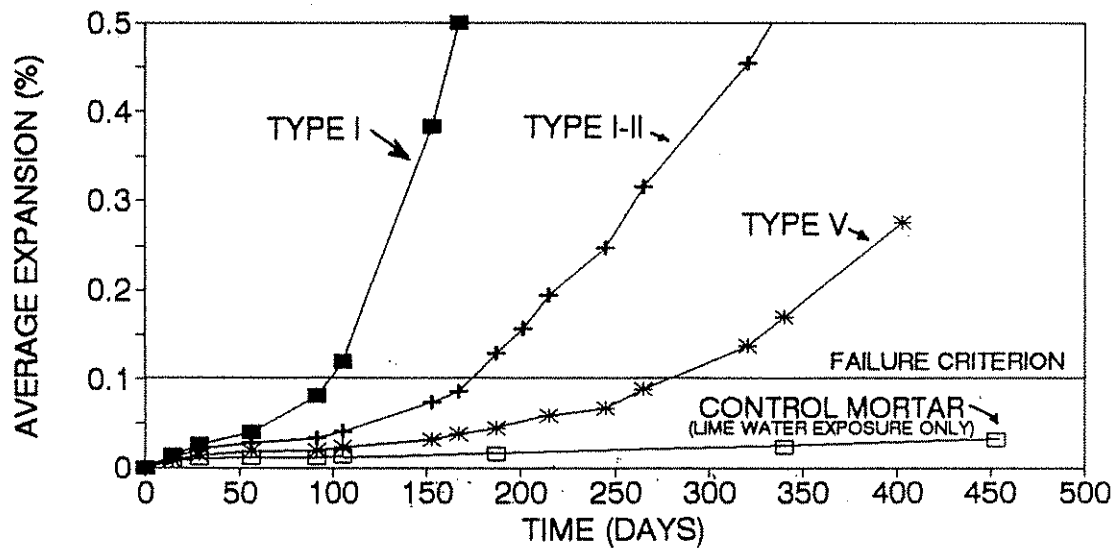
Element	Sample				
	Reagent Grade		Technical Grade		Lyons Rock Salt
	NaCl	Na <sub>2</sub> SO <sub>4</sub>	NaCl	Na <sub>2</sub> SO <sub>4</sub>	
Sr	9	14	16	18	280
Br	61	< 10	100	< 10	N/M
Mg	0.02%	< 50	70	0.02%	0.08%
Fe	50	50	50	60	300
Ca	< 10	85	0.17%	30	0.92%
K	30	20	0.01%	0.02%	0.02%
Ti	17	12	17	16	30
Ba	< 10	< 10	< 10	< 10	< 10
Cl	N/M	40	N/M	0.22%	N/M
I	< 10	< 10	< 10	< 10	< 10
Si	< 50	< 50	< 50	< 50	0.17%
S	70	N/M	0.12%	N/M	0.62%
P	< 10	< 10	< 10	< 10	16
Al	65	60	< 50	< 50	0.06%

N/M = not measured

### **Sulfate Durability Tests - Mortar Bar Specimens**

Typical results obtained from the ASTM C 1012 mortar bar tests are shown in Figure 11. 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 Tables 12 and 13. Not all of the test specimens have reached failure in either of the two test solutions that were used in this study (i.e., 5 percent sodium sulfate and the synthetic deicer solution). To date, 94 percent of the specimens in the 5 percent sodium sulfate solution have

## 5% SULFATE SOAK TEST PORTLAND CEMENT MORTARS



## SYNTHETIC DEICER SOAK TEST PORTLAND CEMENT MORTARS

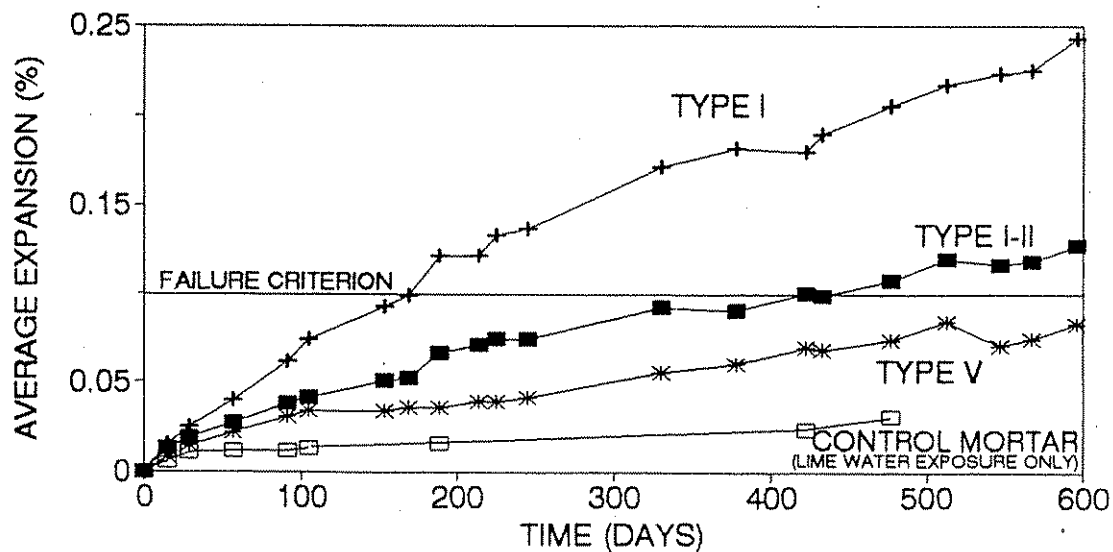


Figure 11. Typical test results that were obtained from the sulfate durability study.

**Table 12. Time (in days) required for mortar bar specimens to reach 0.10 percent expansion.**

Treatment = 5 percent Na <sub>2</sub> SO <sub>4</sub> soak (as per ASTM C 1012)				
Fly Ash	% Replacement	Days to 0.1% Expansion		
		Cement Type		
		Type I	Type I-II	Type V
None	0	98	174	279
Clinton	7.5	92	321	469
	15	153	553	855
	22.5	151	> 950*	> 950*
	30	549	> 950*	> 950*
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 13. Time (in days) required for mortar bar specimens to reach 0.10 percent expansion.

Treatment = synthetic deicer soak (9.5 percent NaCl, 0.25 percent Na <sub>2</sub> SO <sub>4</sub> )				
Fly Ash	% Replacement	Days to 0.1% Expansion		
		Cement Type		
		Type I	Type I-II	Type V
None	0	170	423	705
Clinton	7.5	250	567	746
	15	461	476	> 950*
	22.5	570	768	852
	30	639	742	939
Louisa	7.5	208	456	687
	15	294	478	620
	22.5	453	539	664
	30	555	519	585
Ottumwa	7.5	165	293	584
	15	230	315	592
	22.5	342	474	670
	30	458	437	662
Neal 4	7.5	188	292	637
	15	303	468	511
	22.5	425	573	707
	30	452	458	689
Council Bluffs	7.5	183	300	571
	15	263	370	577
	22.5	301	462	560
	30	422	406	628

\* = test still in progress

failed, as have 98 percent of the specimens in the synthetic deicer solution. Only specimens containing Clinton fly ash and Type I-II or Type V cements currently remain in the testing program, these test specimens have been in the solution for more than 2.5 years.

Figures 12 through 16 depict the failure information in a graphical manner. All of the figures were constructed by plotting the relative durability ratio (RDR) versus fly ash replacement.

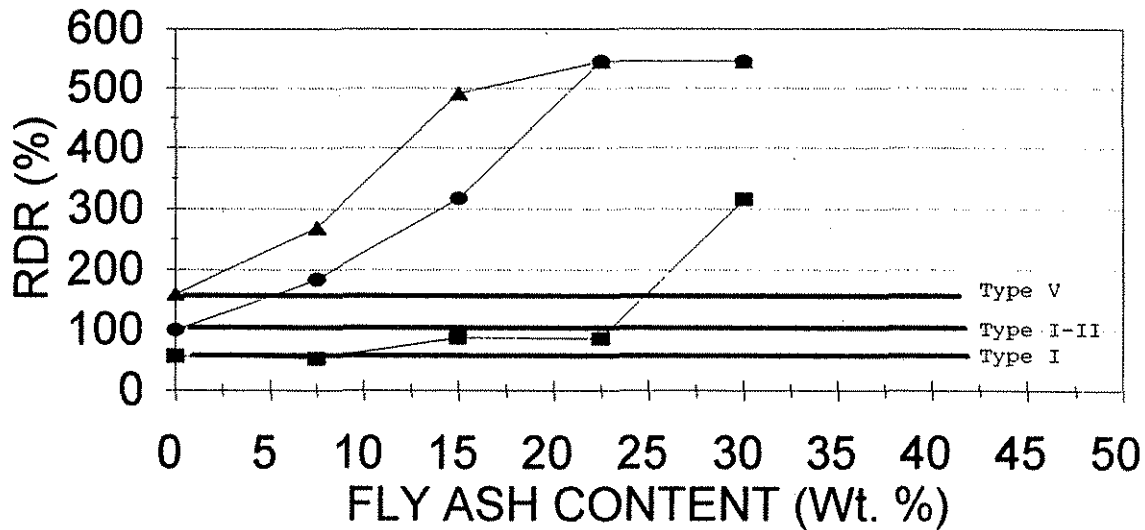
The relative durability ratio (RDR) can be defined as:

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

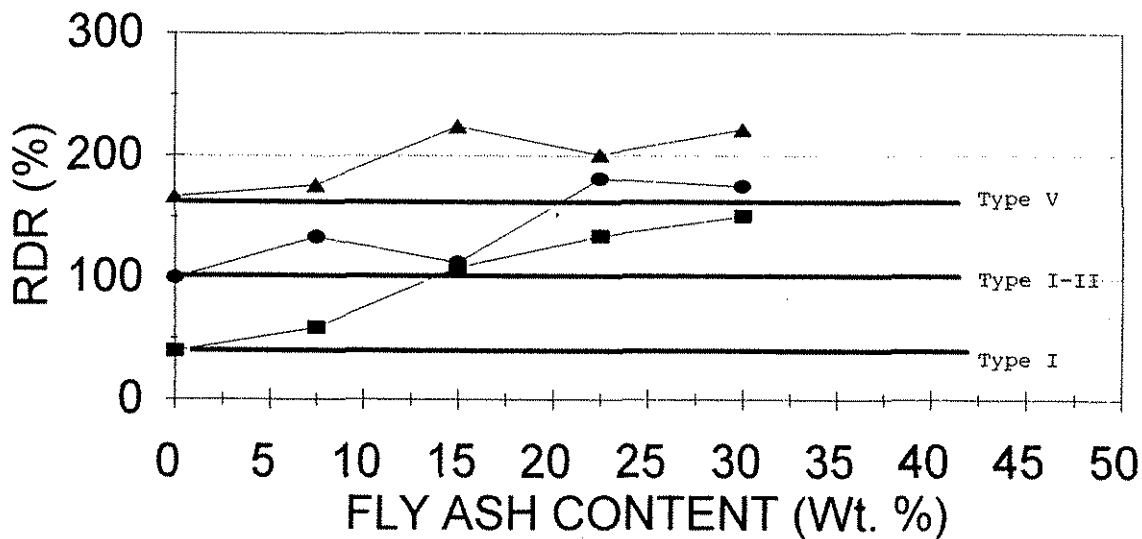
The selection of the Type I-II cement control mortar as the divisor of the RDR equation was arbitrary; however, it seems justifiable because it would be economically unrealistic to compare the test mixtures to the Type V control mortar. Note from Tables 12 and 13, that some of the points plotted on the various figures are only estimates because the specimens had not yet reached the 0.10 percent failure criterion.

Figures 12 through 16 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. 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

### Clinton ASH -- 5% SULFATE SOAK



### Clinton ASH -- SYNTHETIC DEICER SOAK

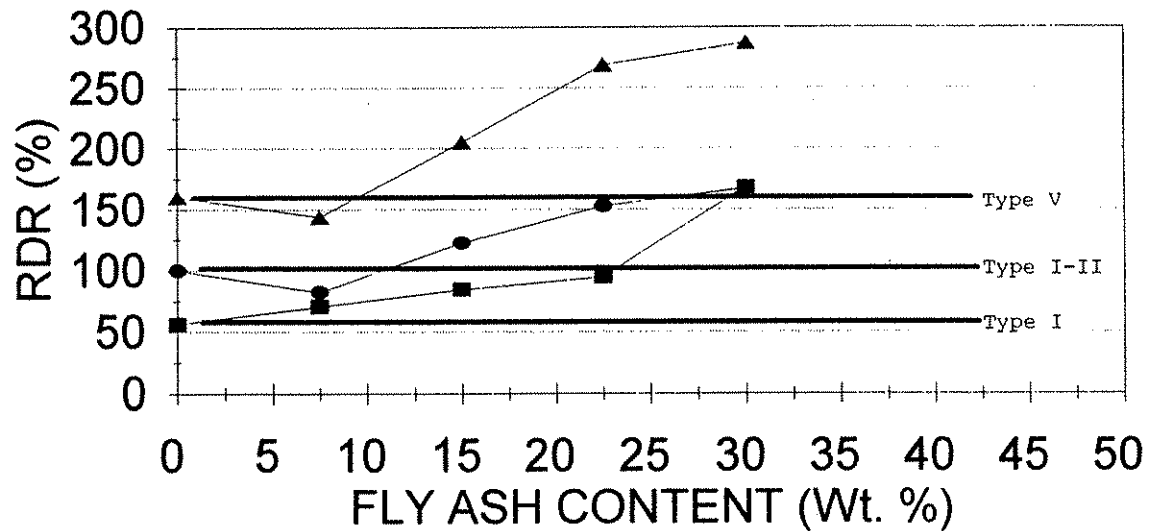


■ TYPE I    ● TYPE I-II    ▲ TYPE V

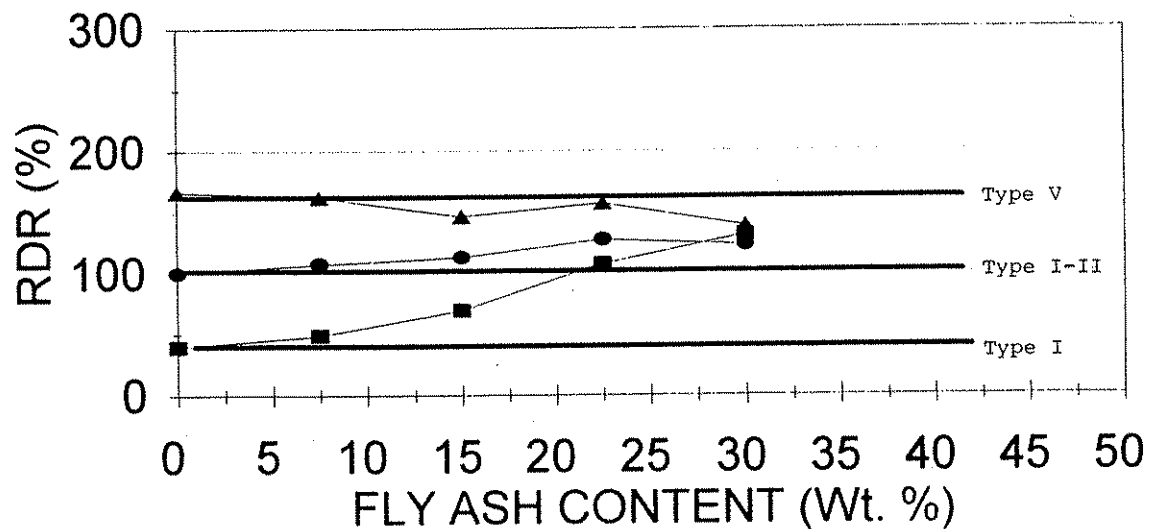
Figure 12. Relative durability ratio (RDR) versus fly ash replacement for Clinton fly ash (Class F).



### Louisa ASH -- 5% SULFATE SOAK



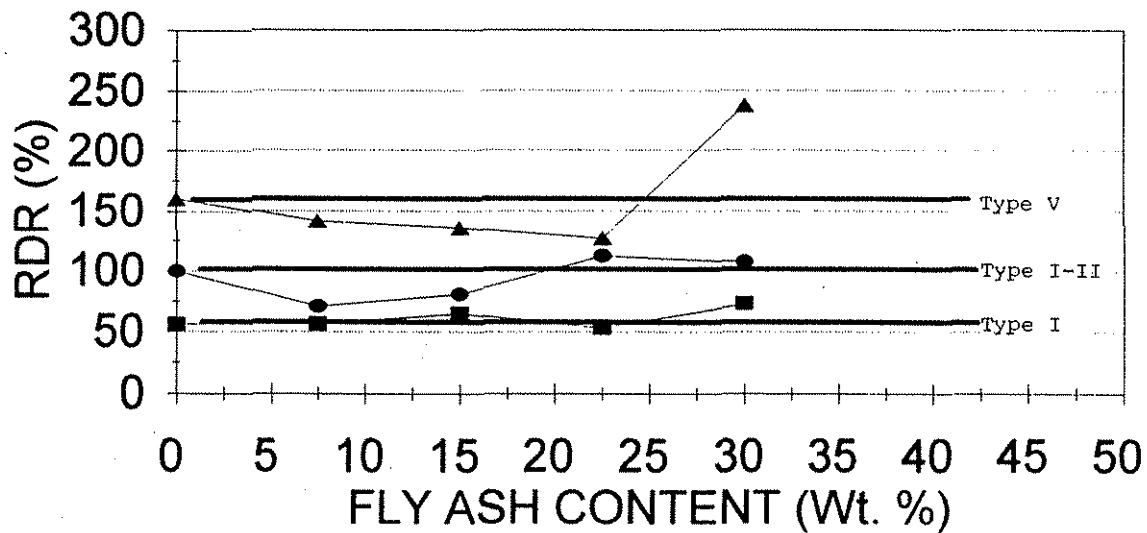
### Louisa ASH -- SYNTHETIC DEICER SOAK



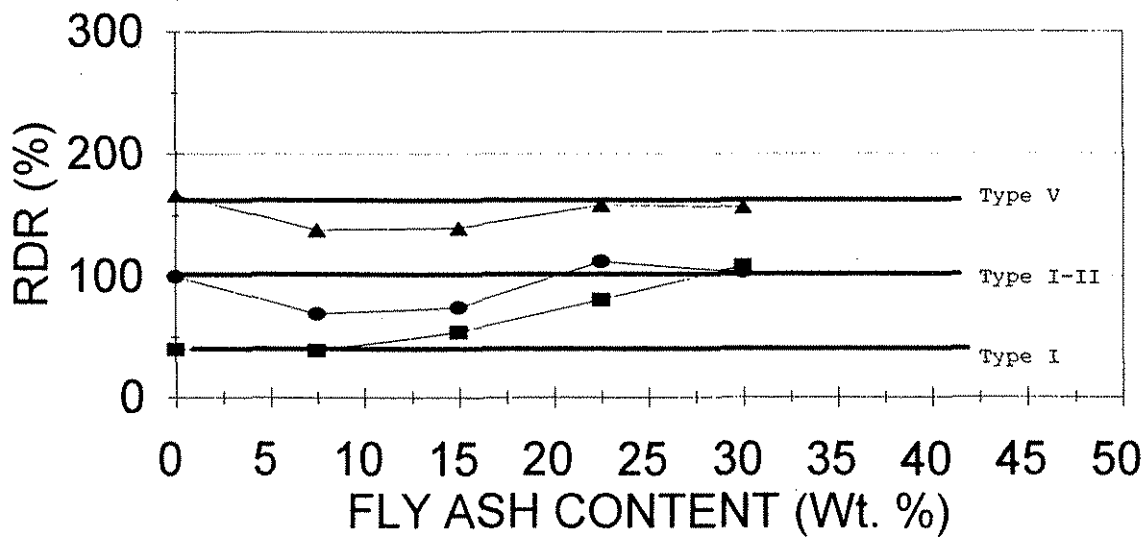
■ TYPE I    ● TYPE I-II    ▲ TYPE V

Figure 13. Relative durability ratio (RDR) versus fly ash replacement for Louisa fly ash (Class C).

### Ottumwa ASH -- 5% SULFATE SOAK



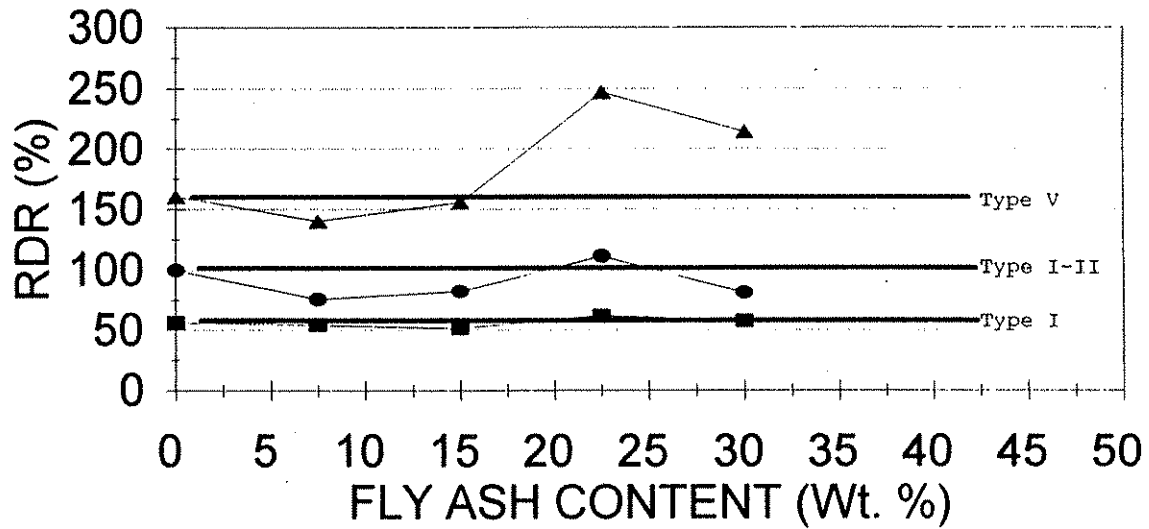
### Ottumwa ASH -- SYNTHETIC DEICER SOAK



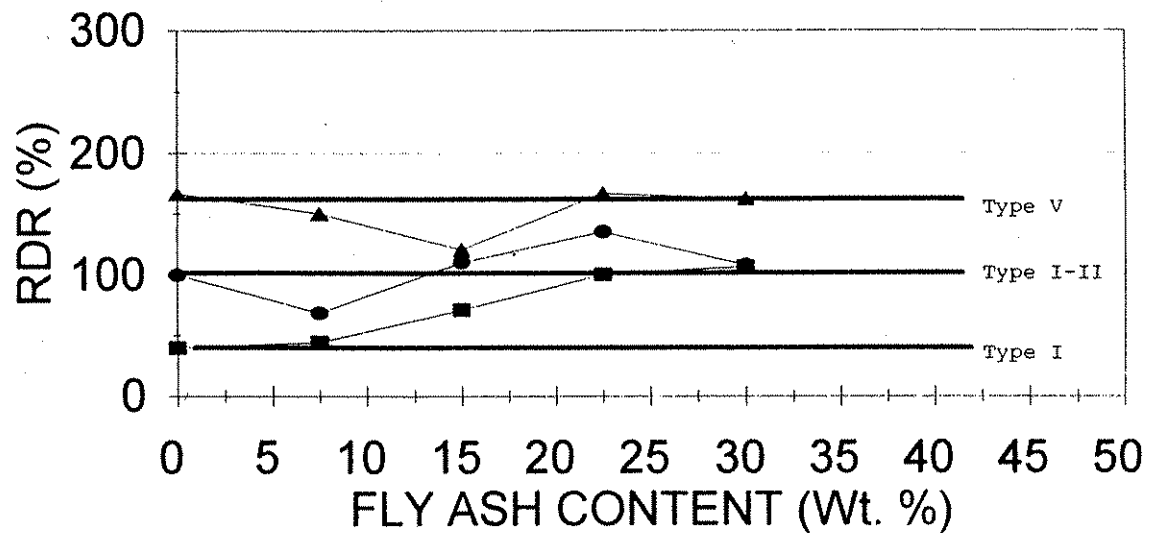
■ TYPE I    ● TYPE I-II    ▲ TYPE V

Figure 14. Relative durability ratio (RDR) versus fly ash replacement for Ottumwa fly ash (Class C).

### Neal 4 ASH -- 5% SULFATE SOAK



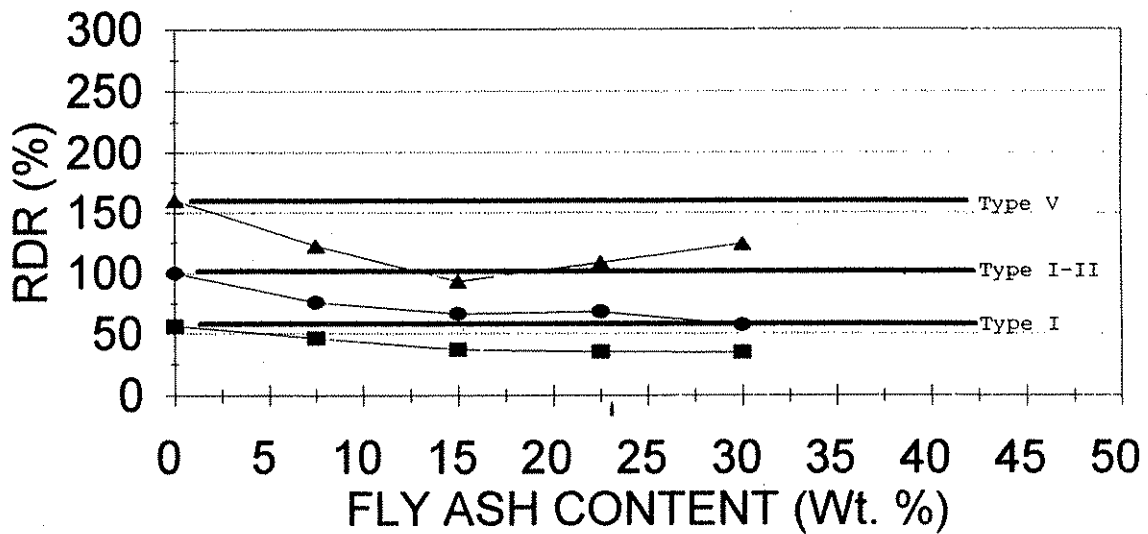
### Neal 4 ASH -- SYNTHETIC DEICER SOAK



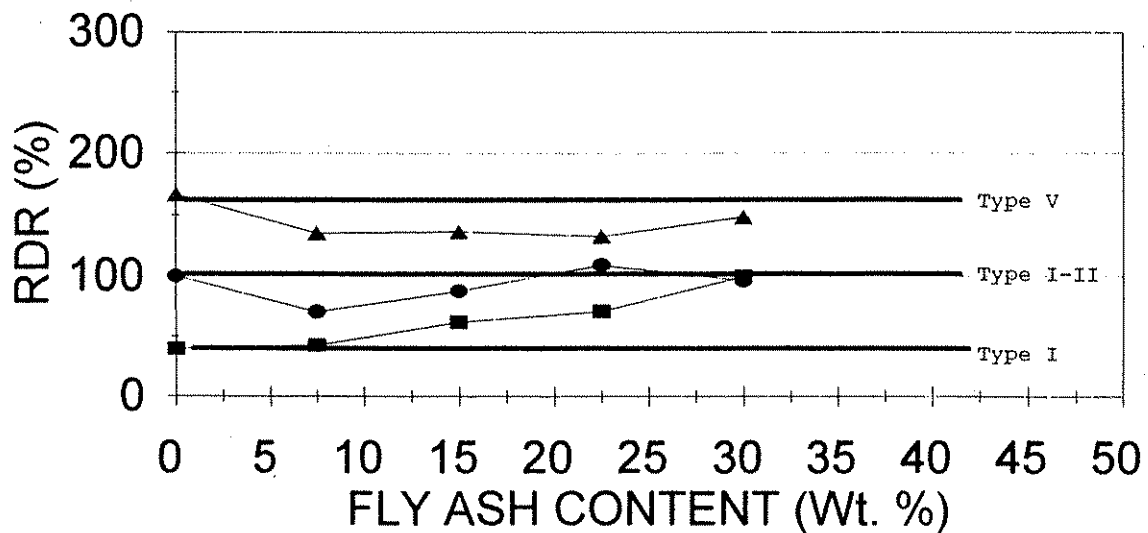
■ TYPE I    ● TYPE I-II    ▲ TYPE V

Figure 15. Relative durability ratio (RDR) versus fly ash replacement for Neal 4 fly ash (Class C).

### Council Bluffs ASH -- 5% SULFATE SOAK



### CBF ASH -- SYNTHETIC DEICER SOAK



■ TYPE I    ● TYPE I-II    ▲ TYPE V

Figure 16. Relative durability ratio (RDR) vs. fly ash replacement for Council Bluffs fly ash (Class C).

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 12 through 16, top portion of each figure) indicate that Clinton and Louisa fly ashes 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 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). Also, increasing fly ash content tended to increase the durability of most of the test specimens (compare the top and bottom halves of Figures 12 through 16). 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. This test procedure (i.e., the synthetic deicer soak test) should be a more realistic simulation of field conditions; and hopefully, a more realistic estimate of field performance.

Many of the mortar specimens were subjected to chemical analysis after they were removed from the treatment tanks. 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. Test

specimens were removed from the synthetic deicer solution after they had expanded about 0.3 percent. These clarifications of testing procedure are important because the chemical testing was only conducted on specimens that had 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.

The mortar specimens that had been removed from the sulfate baths were subjected to XRD and TG analysis. These two test methods were used because they tend to complement one another. However, TG analysis tends to be much more sensitive to minor changes in the concentration of the various hydrates formed in the mortars. Also, it does not rely on the crystallinity of the material; and hence, it can be used to identify and quantify compounds that are amorphous to x-rays.

The results of the XRD and TG study indicated that the mortars had experienced severe sulfate attack. The test results have been summarized in Table 14. The x-ray diffractograms and TG

**Table 14. Summary of results of XRD and TG investigations on the failed mortar specimens.**

<b>Mortar Test Specimens</b>	<b>Solution Type</b>	<b>Compounds Identified</b>	<b>Failure Mechanism</b>
Control (I, I-II, V)	5% sulfate	gypsum, ettringite, portlandite	mixed mode*
Fly Ashes	5% sulfate	ettringite, monosulfoaluminate, gypsum, portlandite	sulfoaluminate corrosion
Control (I, I-II, V)	synthetic deicer	ettringite, portlandite, Friedel's salt	sulfoaluminate corrosion
Fly Ashes	synthetic deicer	Friedel's salt, ettringite, portlandite	sulfoaluminate corrosion

\* mixed mode failure mechanism refers to a combination of both sulfoaluminate corrosion and gypsum corrosion

curves obtained from the various failed test specimens are located in Appendix D. Most of these test results have been discussed in detail in a previous report [30] and, for brevity, will not be reiterated here. The compounds that were identified in the many different specimens were quite similar (see Table 14). Typically only the relative proportions of the various compounds differed between the different mortar specimens. These differences should only be interpreted in a qualitative manner because the process of removing a paste sample from any given mortar specimen may have an

associated sampling error that should be dependent on the hardness of the cement matrix. However, there are some specific trends in the test results that seem to suggest that the failure mechanism in the fly ash mortars can be attributed to sulfoaluminate corrosion. This interpretation is strongly linked to the failures of mortar specimens containing Council Bluffs fly ash. These particular specimens failed rapidly and were immediately removed from the sulfate tanks for analysis. Most of the other specimens failed slowly (over a time period measured in weeks or months, rather than days); and hence, the mortar specimens may have been altered (i.e., more gypsum formation) during the late stages of failure. The poor performance of the high-calcium fly ashes (especially Council Bluffs ash) in the 5 percent sodium sulfate soak test appears to be directly related to the amount monosulfoaluminate (an AF(m) phase) that was formed in the mortar specimen.

Chemical analysis (XRD and TG) was also performed on mortar bar specimens that had been submerged in the synthetic deicer solution. Visual inspection of these mortar bar specimens indicated little evidence of any physical deterioration; however, all of the test specimens had expanded well over 0.1 percent. The phases identified in the specimens were similar to those that were encountered in the sulfate soak test specimens. However there was one important difference. The AF(m) phase (monosulfoaluminate) that was linked to the sulfoaluminate failure mechanism in the 5 percent sulfate soak specimens was not present in any of the test specimens subjected to the synthetic deicer solution. Instead, a different AF(m) phase, commonly referred to as Friedel's salt ( $\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ ), was present in the mortar bar specimens. The concentration of Friedel's salt appeared to increase with increasing fly ash content (for Class C ashes only). Also, no gypsum was identified in any of the test specimens. Hence, since ettringite was present in the specimens, one may conclude that the slow expansive reaction that occurred can be attributed to sulfoaluminate corrosion. Other researchers have reported that chloraluminate AF(m) phases tend to be stable and do not deteriorate under the test environment that was used in this study [32].

### **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 ( $23 \pm 2^\circ\text{C}$ ). 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 [3] were used to evaluate the compressive strength of the different mortar mixes. The results of the tests are summarized in Table 15.

**Table 15. Compressive strength of C109 mortar cubes for 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	6090
Type I	CBF	30	2730	3660	5550
Type I	CLI	15	2080	3220	4980
Type I	CLI	30	1650	2320	4400
Type I-II	None	0	2950	3870	4940
Type I-II	CBF	15	2850	4270	4830
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 16. 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. The interesting aspect of Table 16 is that the sulfate durability of the various specimens is only weakly linked to compressive strength. In fact, the correlation appears to be slightly negative for mortars containing



**Table 16. Results of the curing study sulfate durability tests.**

Cement	Fly Ash	% Replacement	Days to 0.1 % expansion		
			2-day plastic	7-day lime	28-day lime
Type I	None	0	77	90	103
Type I	CBF	15	85	84	51
Type I	CBF	30	96	77	57 <sup>a</sup>
Type I	CLI	15	159	232	222
Type I	CLI	30	330	560	556
Type I-II	None	0	187	154	172
Type I-II	CBF	15	139	141	151
Type I-II	CBF	30	156	101	142
Type I-II	CLI	15	501	502	502
Type I-II	CLI	30	> 770*	> 770*	> 700*

\* = test still in progress

<sup>a</sup> = specimens broke at 50 and 65 days of exposure

Council Bluffs fly ash (i.e., higher strengths correspond to poorer sulfate durability). At first this seems odd; however, after some thought one can conclude that strength has little to do with sulfate durability. Instead, one must concentrate on the chemistry and the porosity (permeability) of the mortar specimens. Since neither of these two variables were specifically measured in this phase of the study one may consider the following explanation for this behavior as speculative at this time.

First, the behavior of the series of control mortars suggests that the porosity of the lean mortar specimens did not change drastically during the three different curing methods. Hence, the sulfate solutions were able to penetrate into the mortar specimens at similar rates and this caused the specimens that had been subjected to different curing methods to fail at similar ages.

Secondly, the chemical information that was discussed earlier in this report has indicated that Council Bluffs fly ash tends to cause more monosulfoaluminate to form in the mortar specimens. However, the monosulfoaluminate can not form immediately because the pore solution is typically saturated with sulfate anions for about the first two days after mixing. This fact, coupled with the

speculation that the porosity of the lean mortar specimens did not change drastically during the different curing processes, leads one to surmise that we have "set up" our test specimens for failure because we have accentuated the formation of monosulfoaluminate in the test specimens by using a lime-water curing process. It is pertinent to point out that all laboratory sulfate durability tests are basically static test methods because they arbitrarily adopt a single curing regime for all of the test specimens. The information listed in Table 16 suggests that these static tests may often oversimplify the dynamic processes that are innate to the hydration reactions that dominate the chemistry of portland cement based materials.

### **Concentration Study**

The purpose of the concentration study was to evaluate the sensitivity of the mortar test specimens to different concentrations of aqueous salt solutions. The soluble salts that were used in the study are summarized in Table 17. The mortar specimens were made using two different cements

**Table 17. Summary of salts used in the concentration study.**

<b>Tank No.</b>	<b>Description of Solution</b>	<b>Concentration (weight %)</b>
1	Lyons Rock Salt (road salt)	20%
2	Lyons Rock Salt (road salt)	10%
3	Sodium Sulfate (Reagent grade)	10%
4	Sodium Sulfate + Sodium Chloride	5% Na <sub>2</sub> SO <sub>4</sub> + 1% NaCl
5	Sodium Sulfate + Sodium Chloride	2.5% Na <sub>2</sub> SO <sub>4</sub> + 2.5% NaCl

(Type I and Type I-II) and four different fly ashes (Clinton, Louisa, Ottumwa and Council Bluffs).

Only two different replacement levels, 15 and 30 percent (by weight), were used in the study. All the test specimens were cured for three days (1 day humid cure, 2 days lime-saturated water) prior to being placed in the various sulfate bearing solutions.

The results of the concentration study are listed in Table 18. Many of the test specimens have not yet failed so it is difficult to make any quantitative statements concerning the influence of the various solutions on sulfate durability. However, the general trend is as one would expect, increasing

**Table 18. Results of the Concentration Study.**

Cement	Fly Ash	% Replacement	Days to 0.1 % Expansion				
			20% Rock Salt	10% Rock Salt	10% Sodium Sulfate	5% Na <sub>2</sub> SO <sub>4</sub> 1% NaCl	2.5% Na <sub>2</sub> SO <sub>4</sub> 2.5% NaCl
Type I	None	0	*	*	66	104	151
Type I	OTT	15	*	*	130	162	*
Type I	OTT	30	*	*	134	*	166
Type I	LOU	15	*	*	140	*	*
Type I	LOU	30	*	*	159	*	*
Type I	CBF	15	*	*	49	147	164
Type I	CBF	30	*	*	105	*	*
Type I	CLI	15	*	*	88	*	*
Type I	CLI	30	*	*	176	*	*
Type I-II	None	0	*	*	170	*	*
Type I-II	OTT	15	*	*	67	110	*
Type I-II	OTT	30	*	*	183	*	*
Type I-II	LOU	15	*	*	186	*	142
Type I-II	LOU	30	*	*	*	*	*
Type I-II	CBF	15	*	*	65	149	183
Type I-II	CBF	30	*	*	114	*	*
Type I-II	CLI	15	*	*	145	*	*
Type I-II	CLI	30	*	*	*	*	*

\* = not available at current age ( $\approx$  200 days)

sulfate concentration tends to accelerate the degradation of the test specimens. This trend is illustrated in Figure 17 for the Type I control cement. It is not currently possible to check the data listed in Table 17 to see if there is an interaction effect between sodium sulfate and sodium chloride. However, this information will be available as soon as all the test specimens reach the failure criterion.

#### **Sulfate Durability Testing - Paste Study**

Some of the results of the paste testing program are illustrated in Figure 18. Note that the

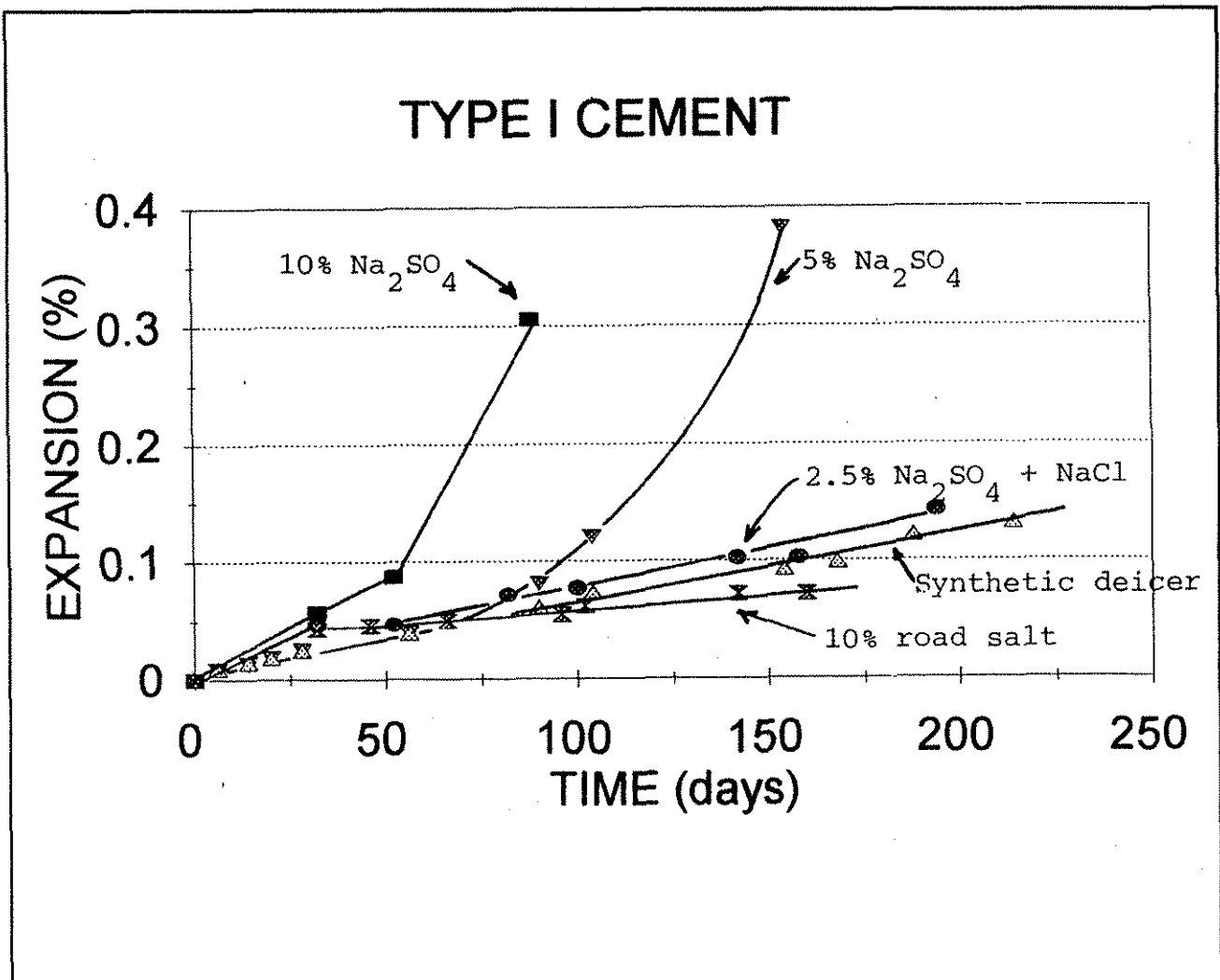
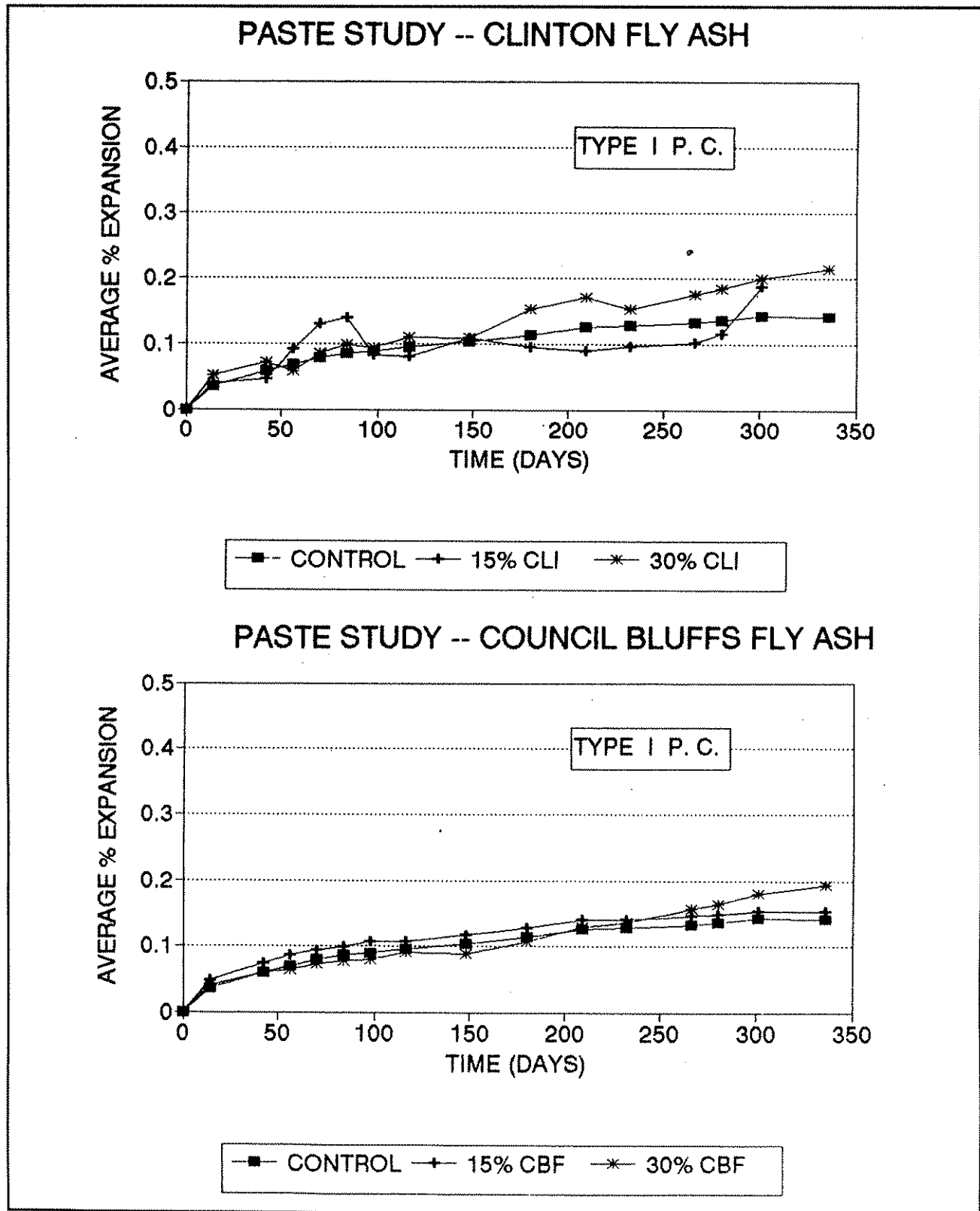
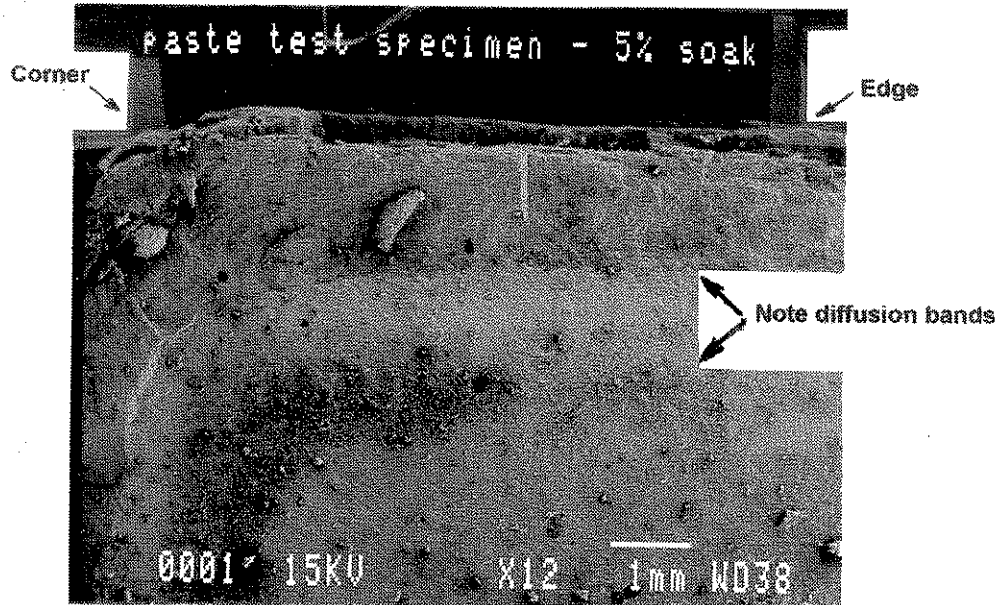


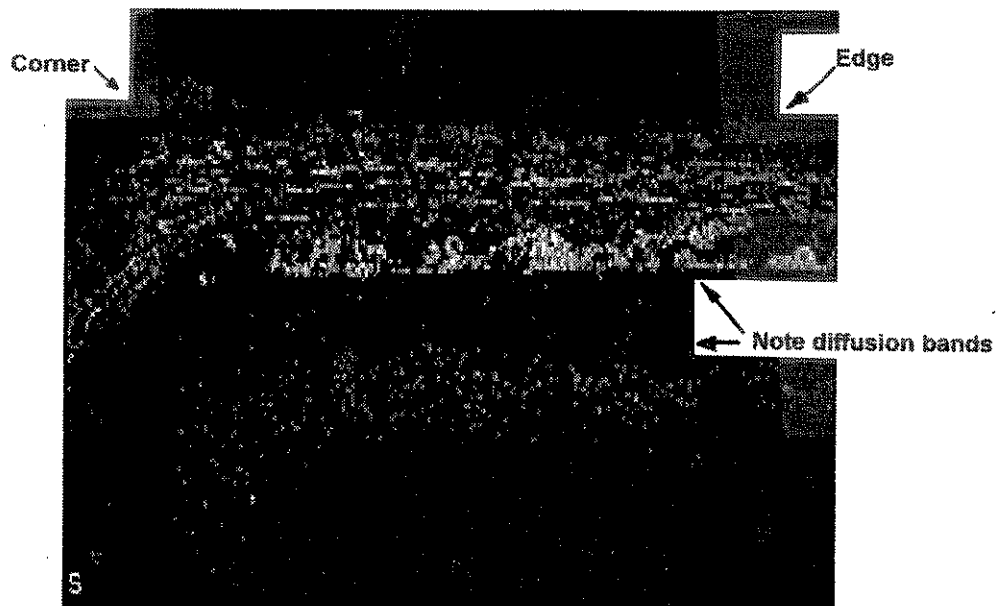
Figure 17. Expansion vs. time for test specimens subjected to different concentrations of sulfate bearing solutions.

specimens only expanded slowly over the duration of the study. Also, note that the Council Bluffs (high-calcium) Class C ash performed as well as the Clinton fly ash (Class F). This is in direct contradiction of the mortar studies. The mortar studies indicated that the Council Bluffs ash tended to cause failure to occur much earlier than the Clinton ash. However, this discrepancy can probably be attributed to the fact that the paste specimens were molded at a low water/cement ratio ( $w/c = 0.35$ ). This low water/cement ratio drastically reduced the porosity of the test specimens and did not allow the sulfate solution to penetrate deeply into the paste specimens. Evidence for this hypothesis is given in Figure 19. Note the diffusion boundary that on the test specimen shown in Figure 19. Increasing the





Secondary electron image of paste specimen.



Sulfur map of the paste specimen.

Figure 19. Diffusion rim in a paste test specimen (Dundee cement, 30% Council Bluffs fly ash).

water/cement ratio of the paste test specimens would also increase their porosity; and hence, test results may approach those of the mortar studies. However, this is not possible from a practical standpoint because the high water/cement ratio test specimens tend to be extremely fluid and bleed excessively.

### **Sulfate Durability Tests - Concrete Study**

A summary of the details pertaining to the concrete mixes made by Iowa Department of Transportation personnel is listed in Table 19. All of the concrete mixes had air contents of  $6 \pm 1$  percent and slumps of  $2 \pm 0.5$  inches. The 28-day compressive strengths of the different mixes varied from a low of about 5000 psi (typically mixes containing Clinton ash, Class F) to a high of over 7000 psi for several of the moderate to high replacement mixes containing Class C ashes.

The current test results for the various concrete mixes that have been subjected to the sulfate test solutions, 10 percent sodium sulfate and the synthetic deicer solution (containing 9.5 percent sodium chloride plus 0.5 percent sodium sulfate), have been summarized in Table 20. The parameters that have been listed include specimen growth (linear expansion) and relative dynamic modulus of elasticity (RDM). The mass of the various test specimens was also monitored during the study but all of the test specimens are currently within one percent of their initial mass.

Several details need to be discussed concerning Table 20. First, none of the test specimens have yet reached the failure criterion of 0.1 percent expansion. In fact, if the failure criterion was reduced to 0.05 percent expansion then only two percent of the test specimens would have failed, and they would all consist of Type I portland cement control specimens. Hence, all the discussion that follows must be considered as "preliminary" and may be subject to significant change as the tests progress. Secondly, the growth values and RDM values tend to be in agreement with one another, and they tend to indicate reasonably sound concrete. Typically the growth values decreased with increasing fly ash content. And finally, the growth and RDM values for the specimens subjected to the 10 percent sulfate soak test are typically quite similar to the specimens that were subjected to the synthetic deicer soak test. However, the visual appearance of these two different groups of test specimens was very dramatic. The test specimens submerged in the synthetic deicer

Table 19. Summary of concrete mix parameters.

Coarse Aggregate: Jabens								
Mix #	Cement	Fly Ash	Ash %	Water/ Cement	Air %	Slump (inches)	Unit Wt. (pcf)	28-day Comp. Str. (psi)
1	Dundee	None	0	0.462	5.9	1.75	143.6	6620
2		Ottumwa	7.5	0.464	6.1	2.00	143.2	-
3			15	0.439	5.9	1.75	143.2	6710
4			30	0.413	5.8	2.25	143.6	6480
5	Dundee	C. Bluffs	7.5	0.446	6.0	2.00	143.6	-
6			15	0.429	5.8	2.00	144.8	7150
7			30	0.413	6.3	1.75	143.2	6440
8	Dundee	Clinton	7.5	0.464	6.1	2.25	142.0	-
9			15	0.453	5.7	1.75	143.6	6590
10			30	0.451	5.6	1.75	143.6	6130
11	S. Dakota	None	0	0.472	6.0	2.00	143.6	6490
12		Ottumwa	7.5	0.470	6.0	2.25	143.2	-
13			15	0.453	5.9	2.00	144.0	7130
14			30	0.422	6.0	1.75	143.6	6990
15	S. Dakota	C. Bluffs	7.5	0.458	6.1	2.00	143.2	-
16			15	0.429	5.8	1.75	144.4	6880
17			30	0.418	6.5	1.75	142.8	6930
18	S. Dakota	Clinton	7.5	0.464	6.4	2.25	143.2	-
19			15	0.453	6.3	2.25	141.6	6580
20			30	0.446	5.7	2.00	142.2	6380
21	Dundee	Louisa	7.5	0.458	6.2	1.75	143.6	-
22			15	0.434	6.0	2.00	144.0	7040
23			30	0.422	6.0	2.25	144.0	7230
24	S. Dakota	Louisa	7.5	0.458	5.9	2.25	143.2	-
25			15	0.448	6.0	2.25	143.2	6550
26			30	0.432	6.0	2.00	144.0	7280



Table 19. Summary of concrete mix parameters (continued)

Coarse Aggregate: Lamont								
Mix #	Cement	Fly Ash	Ash %	Water/ Cement	Air %	Slump (inches)	Unit Wt. (pcf)	28-day Comp. Str. (psi)
27	Dundee	None	0	0.481	6.2	2.00	143.6	6440
28		Ottumwa	7.5	0.452	6.6	2.00	142.8	-
29			15	0.439	6.8	2.00	142.8	6210
30			30	0.413	6.8	2.00	143.6	6610
31	Dundee	C. Bluffs	7.5	0.458	6.7	2.25	142.8	-
32			15	0.434	6.2	2.00	144.8	7370
33			30	0.418	6.3	2.25	144.8	6790
34	Dundee	Clinton	7.5	0.476	6.5	2.50	142.8	-
35			15	0.458	5.9	2.00	144.8	6330
36			30	0.446	5.8	2.00	144.8	6050
37	S. Dakota	None	0	0.462	6.0	2.00	144.0	6950
38		Ottumwa	7.5	0.464	6.3	2.00	144.4	-
39			15	0.443	6.4	2.25	144.0	7280
40			30	0.423	6.1	2.00	144.8	7750
41	S. Dakota	C. Bluffs	7.5	0.458	6.4	2.00	144.0	-
42			15	0.448	6.4	2.00	144.0	7050
43			30	0.437	6.4	2.00	144.6	7130
44	S. Dakota	Clinton	7.5	0.464	6.4	2.25	143.6	-
45			15	0.448	6.1	1.75	144.4	6690
46			30	0.469	5.8	2.25	144.0	6690
47	Dundee	Louisa	7.5	0.458	6.1	2.25	144.4	-
48			15	0.434	6.1	2.25	145.2	7790
49			30	0.423	5.7	2.25	146.0	6650
50	S. Dakota	Louisa	7.5	0.458	6.1	2.50	144.8	-
51			15	0.440	6.2	2.25	144.8	7310
52			30	0.427	6.0	2.25	145.2	7450

Table 19. Summary of concrete mix parameters (continued)

Coarse Aggregate: Montour								
Mix #	Cement	Fly Ash	Ash %	Water/ Cement	Air %	Slump (inches)	Unit Wt. (pcf)	28-day Comp. Str. (psi)
53	Dundee	None	0	0.439	6.6	2.75	142.0	5920
54		Ottumwa	7.5	0.405	6.8	1.75	143.2	-
			15	0.401	5.6	2.00	144.0	6640
			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	None	0	0.424	5.8	2.25	143.6	6860
67		Ottumwa	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 19. Summary of concrete mix parameters (continued)

Coarse Aggregate: Early Chapel								
Mix #	Cement	Fly Ash	Ash %	Water/ Cement	Air %	Slump (inches)	Unit Wt. (pcf)	28-day Comp. Str. (psi)
79	Dundee	None	0	0.476	5.7	1.75	142.8	5700
80		Ottumwa	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	None	0	0.466	5.5	1.75	143.6	6450
93		Ottumwa	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

Table 20. Summary of concrete mix relative dynamic modulus (RDM) and growth.

Coarse Aggregate: Jabens				AGE: 116 weeks			
Mix #	Cement	Fly Ash	Ash %	10% Sulfate Soak		Synthetic Deicer Soak	
				RDM (%)	Growth (%)	RDM (%)	Growth (%)
1	Dundee	None	0	100	0.056	96	0.046
2		Ottumwa	7.5	101	0.042	99	0.044
3			15	104	0.033	99	0.037
4			30	106	0.028	105	0.024
5	Dundee	C. Bluffs	7.5	101	0.038	99	0.044
6			15	101	0.030	100	0.035
7			30	106	0.027	104	0.028
8	Dundee	Clinton	7.5	104	0.021	99	0.028
9			15	109	0.022	103	0.036
10			30	109	0.018	110	0.018
11	S. Dakota	None	0	102	0.028	100	0.029
12		Ottumwa	7.5	103	0.025	101	0.030
13			15	106	0.027	102	0.019
14			30	107	0.039	104	0.017
15	S. Dakota	C. Bluffs	7.5	103	0.025	102	0.024
16			15	103	0.021	104	0.026
17			30	111	0.019	105	0.024
18	S. Dakota	Clinton	7.5	108	0.016	104	0.022
19			15	107	0.014	103	0.023
20			30	110	0.013	109	0.013
21	Dundee	Louisa	7.5	105	0.031	100	0.031
22			15	108	0.027	102	0.028
23			30	108	0.018	107	0.020
24	S. Dakota	Louisa	7.5	103	0.021	102	0.020
25			15	110	0.016	103	0.023
26			30	114	0.016	111	0.016

Table 20. Summary of concrete mix relative dynamic modulus (RDM) and growth (continued)

Coarse Aggregate: Lamont				AGE: 104 weeks			
Mix #	Cement	Fly Ash	Ash %	10% Sulfate Soak		Synthetic Deicer Soak	
				RDM (%)	Growth (%)	RDM (%)	Growth (%)
27	Dundee	None	0	109	0.073	100	0.030
28		Ottumwa	7.5	110	0.027	107	0.029
29			15	111	0.024	104	0.029
30			30	110	0.021	110	0.021
31	Dundee	C. Bluffs	7.5	108	0.030	102	0.028
32			15	109	0.027	106	0.027
33			30	111	0.032	107	0.024
34	Dundee	Clinton	7.5	108	0.017	106	0.029
35			15	114	0.015	106	0.022
36			30	111	0.015	109	0.016
37	S. Dakota	None	0	107	0.025	103	0.028
38		Ottumwa	7.5	110	0.018	105	0.023
39			15	107	0.016	107	0.018
40			30	108	0.017	109	0.016
41	S. Dakota	C. Bluffs	7.5	110	0.017	102	0.019
42			15	111	0.014	104	0.020
43			30	115	0.018	109	0.019
44	S. Dakota	Clinton	7.5	116	0.012	107	0.002
45			15	114	0.009	107	0.016
46			30	119	0.014	113	0.010
47	Dundee	Louisa	7.5	109	0.028	107	0.026
48			15	109	0.023	109	0.023
49			30	112	0.021	112	0.016
50	S. Dakota	Louisa	7.5	110	0.019	106	0.020
51			15	112	0.014	107	0.027
52			30	114	0.015	112	0.017

Table 20. Summary of concrete mix relative dynamic modulus (RDM) and growth (continued)

Coarse Aggregate: Montour				AGE: 64 weeks			
Mix #	Cement	Fly Ash	Ash %	10% Sulfate Soak		Synthetic Deicer Soak	
				RDM (%)	Growth (%)	RDM (%)	Growth (%)
53	Dundee	None	0	104	0.039	101	0.017
54		Ottumwa	7.5	107	0.019	99	0.020
55			15	103	0.013	106	0.015
56			30	108	0.007	103	0.009
57	Dundee	C. Bluffs	7.5	107	0.023	101	0.017
58			15	106	0.018	103	0.011
59			30	108	0.012	102	0.019
60	Dundee	Clinton	7.5	107	0.014	104	0.013
61			15	108	0.006	103	0.010
62			30	111	0.007	104	0.007
63	Dundee	Louisa	7.5	104	0.018	102	0.011
64			15	104	0.009	102	0.014
65			30	107	0.005	104	0.006
66	S. Dakota	None	0	105	0.006	101	0.009
67		Ottumwa	7.5	106	0.014	101	0.014
68			15	105	0.012	102	0.038
69			30	110	0.006	106	0.006
70	S. Dakota	C. Bluffs	7.5	106	0.009	105	0.009
71			15	104	0.011	102	0.011
72			30	103	0.013	105	0.013
73	S. Dakota	Clinton	7.5	105	0.007	104	0.007
74			15	107	0.003	106	0.005
75			30	109	0.004	108	0.008
76	S. Dakota	Louisa	7.5	103	0.004	103	0.006
77			15	106	0.007	102	0.009
78			30	108	0.004	106	0.003

Table 20. Summary of concrete mix relative dynamic modulus (RDM) and growth (continued)

Coarse Aggregate: Early Chapel				AGE: 52 weeks			
Mix #	Cement	Fly Ash	Ash %	10% Sulfate Soak		Synthetic Deicer Soak	
				RDM (%)	Growth (%)	RDM (%)	Growth (%)
79	Dundee	None	0	107	0.031	106	0.019
80		Ottumwa	7.5	109	0.020	105	0.017
81			15	108	0.014	105	0.014
82			30	107	0.012	106	0.011
83	Dundee	C. Bluffs	7.5	109	0.020	102	0.016
84			15	106	0.016	103	0.019
85			30	109	0.010	103	0.013
86	Dundee	Clinton	7.5	109	0.004	98	0.012
87			15	110	0.007	105	0.010
88			30	111	0.007	108	0.006
89	Dundee	Louisa	7.5	109	0.011	104	0.014
90			15	108	0.019	106	0.008
91			30	111	0.006	110	0.013
92	S. Dakota	None	0	109	0.004	107	0.006
93		Ottumwa	7.5	109	0.002	109	0.002
94			15	110	0.003	108	0.010
95			30	110	0.004	109	0.005
96	S. Dakota	C. Bluffs	7.5	107	0.002	104	0.017
97			15	108	0.006	105	0.011
98			30	110	0.005	105	0.009
99	S. Dakota	Clinton	7.5	114	0.008	104	0.009
100			15	112	0.002	108	0.004
101			30	115	0.007	109	0.004
102	S. Dakota	Louisa	7.5	108	0.005	102	0.009
103			15	109	0.004	106	0.011
104			30	110	0.002	106	0.006

solution had little or no apparent spalling or cracking. The specimens in the 10 percent sulfate solution had suffered significant deterioration.

Figures 20 through 23 illustrate the typical condition of the specimens that had been subjected to the 10 percent sodium sulfate solution. The concrete specimens containing Montour coarse aggregate and Lamont coarse aggregate exhibited similar trends. In most cases, the specimens appear to be spalling off the outside portion of the concrete. Hence, the beams tend to loose edges first and then they take on a "rounded" appearance. The deterioration is visibly quite evident but, as mentioned earlier, the specimens have lost a negligible amount of mass. Counting the corners on the various test specimens gives a reasonable way to compare the relative level of deterioration. Many of the specimens containing Type I cement and 30 percent fly ash appear to be in better shape than the control specimen containing Type V cement.

#### **Alkali Reactivity Tests - Mortar Bar Studies**

Typical results from the alkali reactivity tests are shown in Figures 24 and 25. These figures illustrate how the various mortar specimens expanded as a function of time. It is pertinent to mention several important details that are evident in the figures.

First, the mortar bar specimens that contained Pyrex glass aggregate expanded more rapidly and to a much greater magnitude than the specimens containing the other two aggregates (Class V or standard sand). Hence, these tests were discontinued after one year of moist curing because the test specimens had stopped expanding (note, in the top half of Figure 24, how flat the expansion-time curves become after approximately three months of curing). This is in agreement with the available alkali study, which indicated that the fly ashes contributed a significant amount of alkalis to the pore solution for about the first three months of curing (compare Figures 10 and 24).

Secondly, test specimens containing the Class V aggregate and the standard (Ottawa) sand aggregate exhibited very similar trends. However, the mortar bars containing the Class V aggregate did tend to expand slightly more than those containing the standard sand. Note in the bottom half of Figure 24, that the scale that was used has changed significantly from that used in the top half of the





Figure 20. Specimens subject to the 10 percent sulfate soak test; Type I cement, various fly ashes at 7.5, 15 and 30 percent replacement, Jaben aggregate, age about 128 weeks.

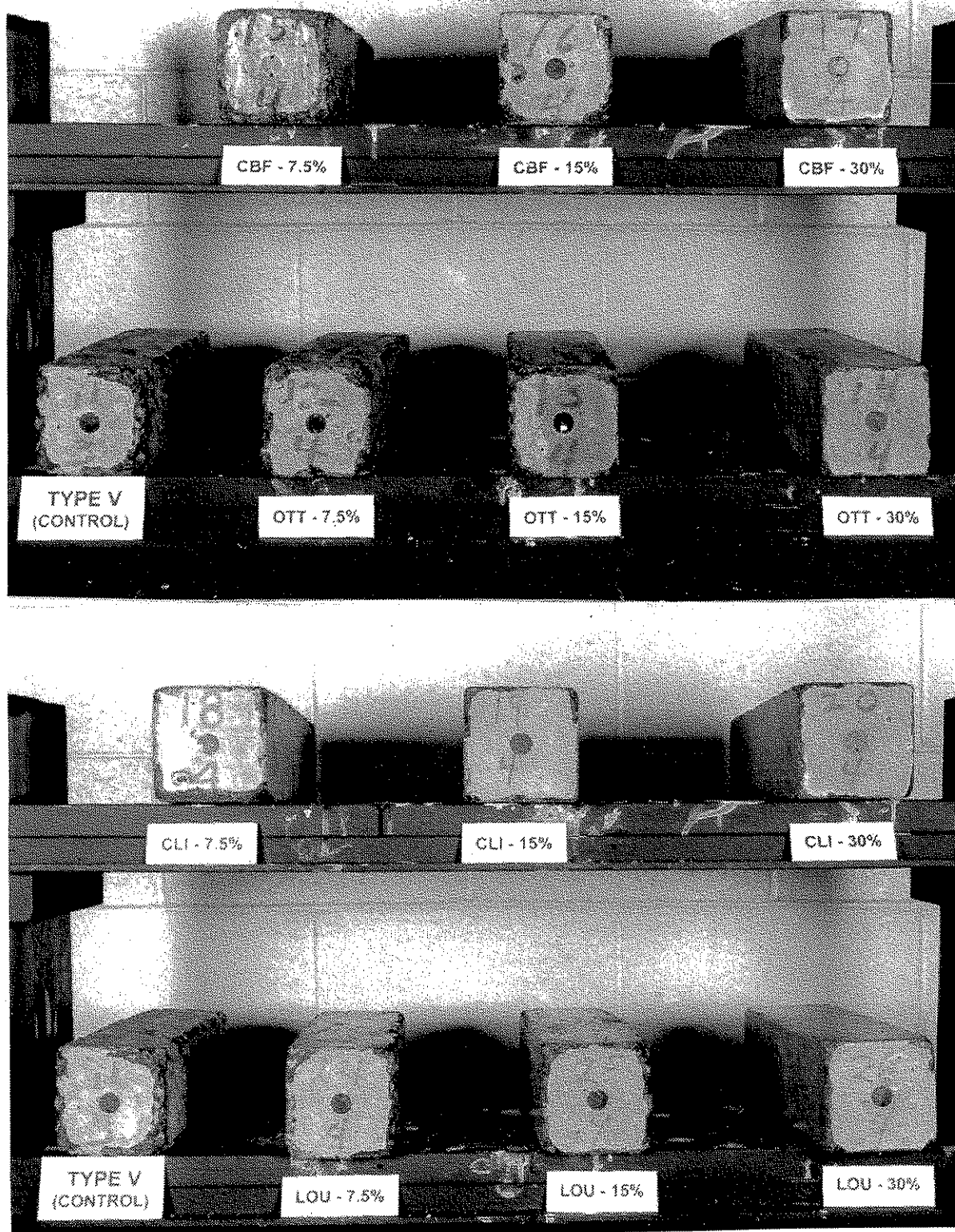


Figure 21. Specimens subject to the 10 percent soak test; Type V cement, various fly ashes at 7.5, 15 and 30 percent replacement, Jaben aggregate, age about 128 weeks.



Figure 22. Specimens subject to the 10 percent sulfate soak test; Type I cement, various fly ashes at 7.5, 15 and 30 percent replacement, Early Chapel aggregate, age about 64 weeks.



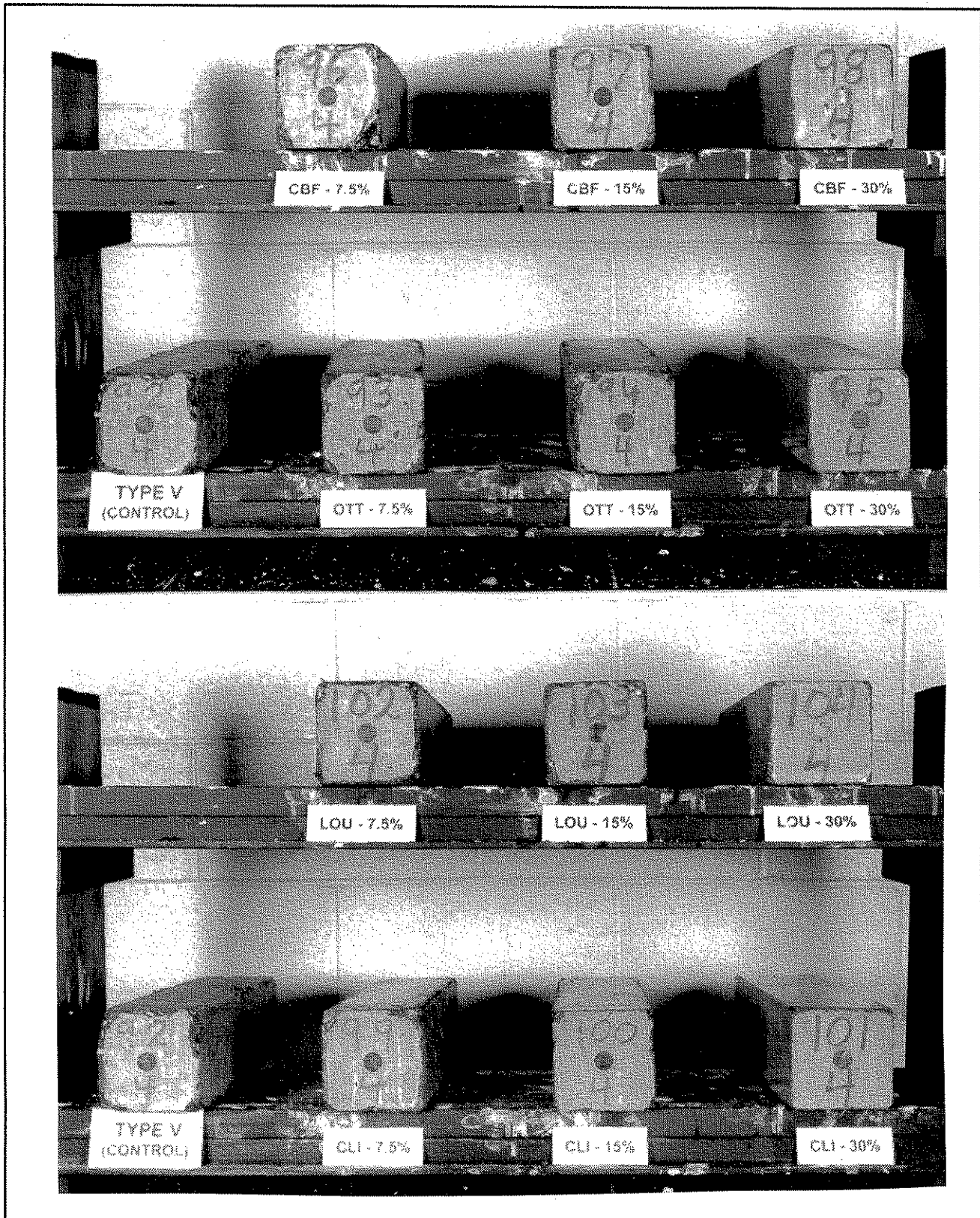


Figure 23. Specimens subject to the 10 percent soak test; Type V cement, various fly ashes at 7.5, 15 and 30 percent replacement, Early Chapel aggregate, age about 64 weeks.

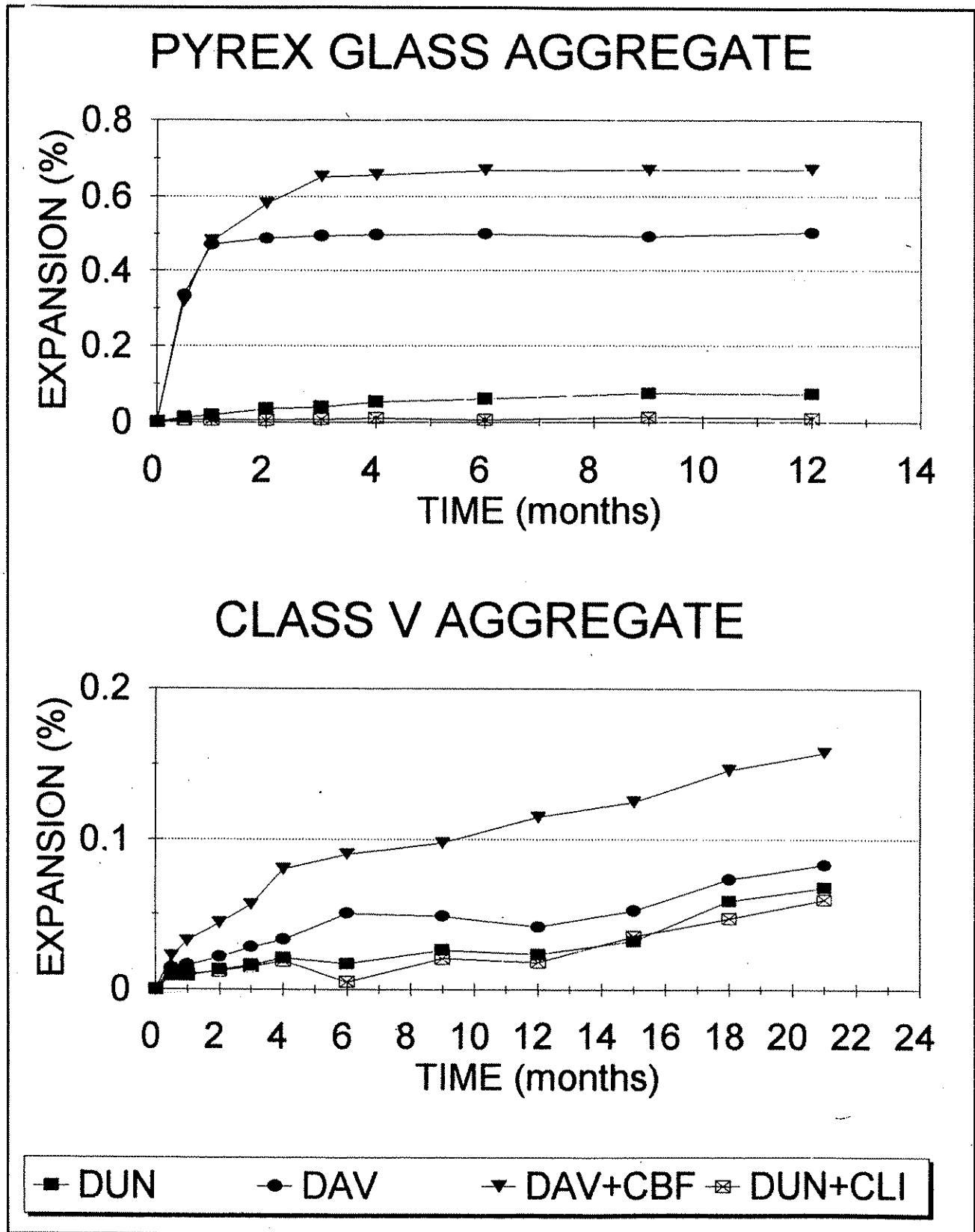
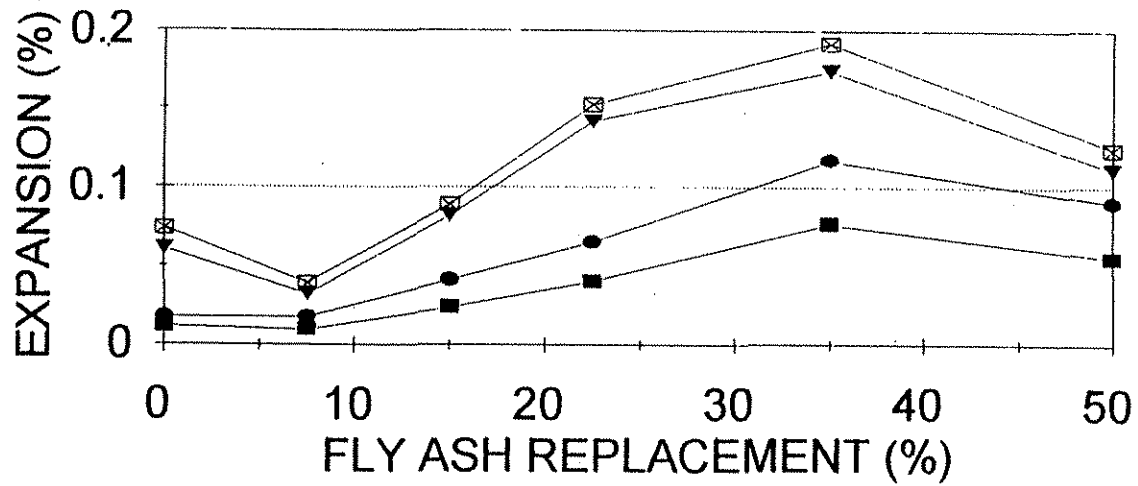


Figure 24. Typical test results that were obtained from the ASR study.

# PYREX -- LOUISA ASH -- DUNDEE



# CLASS V -- LOUISA ASH -- DAVENPORT

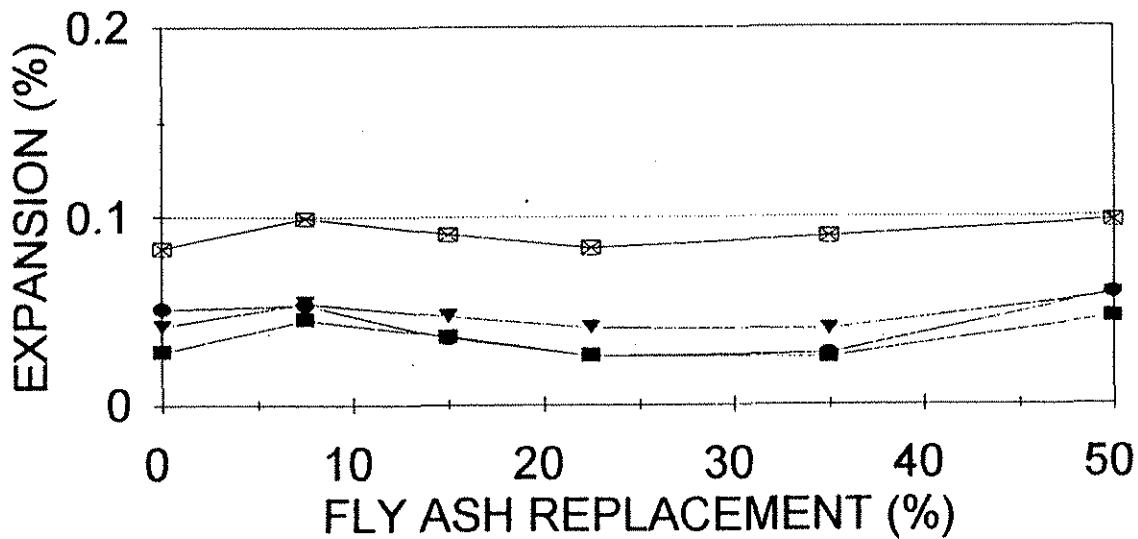


Figure 25. Influence of time on the test results of the ASR study.

figure. The expansion axis has been reduced by a factor of about 3 while the time axis has almost been doubled. Hence, the measured response was small and the duration of the test was very long. This fact was anticipated at the beginning of the research project. Since we are attempting to distinguish small differences between test specimens that exhibited only a small response to the treatment it is very important to know the precision of the test method. This has been estimated for the control specimens by making duplicate test specimens on two different days (actually weeks apart). It has been assumed that the specimens containing fly ash exhibit the same level of precision. These test results are summarized in Table 21. Typically the test results were repeatable to about  $\pm 10$  percent (relative error, coefficient of variation), this corresponds to an absolute error of about  $\pm 0.01$  percent expansion.

Finally, we must remember that the goal of the project was to evaluate how fly ash influences the AAR test results. Since all the testing information varies as a function of time we must pick some arbitrary time for comparing expansion values. For the purpose of this report we have chosen to compare expansion values at 6 months for specimens containing the Pyrex glass aggregate, and at 21 months when comparing the specimens containing the natural aggregates. These selections were arbitrary and, as illustrated in Figure 25, had little influence on the trends exhibited by the test specimens. Hence, future discussion will be limited to the data listed in Table 21.

The expansion values summarized in Table 21 make it easier to show how the various fly ashes influence the alkali-reactivity tests.

Plots of linear expansion versus fly ash content are shown in Figures 26 through 28. These figures illustrate how expansion varied with: {1} the source of the fly ash; {2} the amount of the fly ash that was present in any given mortar mix; and {3} the type of aggregate that was used. The upper half of each figure denotes the test response that was observed when the moderate alkali cement (Davenport, 0.76 percent equivalent sodium oxide) was used. The lower half of each figure denotes the test response that was observed when the low alkali cement (Dundee, 0.39 percent equivalent sodium oxide) was used.

**Table 21. Results of alkali-aggregate reactivity tests conducted on the five fly ashes.**  
**All values listed as percent expansion.**

<b>Pyrex Glass Aggregate, expansion values measured at 6 months</b>					
<b>DUN cement (0.39% equivalent sodium oxide)</b>					
<b>% Fly Ash</b>	<b>Clinton</b>	<b>Louisa</b>	<b>Neal 4</b>	<b>Council Bluffs</b>	<b>Ottumwa</b>
0	0.06	0.06	0.06	0.06	0.06
7.5	0.08	0.03	0.20	0.22	0.28
15	0.01	0.08	0.29	0.41	0.40
22.5	0.01	0.14	0.24	0.52	0.44
35	0.01	0.18	0.25	0.47	0.51
50	0.01	0.11	0.30	0.33	0.30
<b>DAV cement (0.76% equivalent sodium oxide)</b>					
<b>% Fly Ash</b>	<b>Clinton</b>	<b>Louisa</b>	<b>Neal 4</b>	<b>Council Bluffs</b>	<b>Ottumwa</b>
0	0.50	0.50	0.50	0.50	0.50
7.5	0.05	0.49	0.55	0.60	0.52
15	0.01	0.44	0.54	0.51	0.51
22.5	0.12	0.33	0.50	0.67	0.54
35	0.07	0.24	0.41	0.47	0.53
50	0.02	0.14	0.28	0.36	0.24



**Table 21. Results of alkali-aggregate reactivity tests conducted on the five fly ashes (continued)**  
 All values listed as percent expansion.

<b>Class V Aggregate (Oreapolis), expansion values measured at 21 months</b>					
<b>DUN cement (0.39% equivalent sodium oxide)</b>					
<b>% Fly Ash</b>	<b>Clinton</b>	<b>Louisa</b>	<b>Neal 4</b>	<b>Council Bluffs</b>	<b>Ottumwa</b>
0	0.06*	0.06*	0.06*	0.06*	0.06*
7.5	0.07	0.06	0.07	0.06	0.06
15	0.06	0.07	0.06	0.07	0.08
22.5	0.06	0.07	0.06	0.06	0.09
35	0.06	0.07	0.06	0.08	0.08
50	0.06	0.10	0.06	0.10	0.10
<b>DAV cement (0.76% equivalent sodium oxide)</b>					
<b>% Fly Ash</b>	<b>Clinton</b>	<b>Louisa</b>	<b>Neal 4</b>	<b>Council Bluffs</b>	<b>Ottumwa</b>
0	0.08**	0.08**	0.08**	0.08**	0.08**
7.5	0.05	0.10	0.10	0.08	0.09
15	0.05	0.09	0.09	0.11	0.14
22.5	0.08	0.08	0.11	0.14	0.14
35	0.07	0.09	0.08	0.16	0.10
50	0.06	0.10	0.08	0.11	0.12

\* based on n=4 and  $0.062 \pm 0.006$

\*\* based on n=4 and  $0.082 \pm 0.015$

**Table 21. Results of alkali-aggregate reactivity tests conducted on the five fly ashes (continued)**  
 All values listed as percent expansion.

Standard (Ottawa) Sand, expansion values measured at 21 months					
DUN cement (0.39% equivalent sodium oxide)					
% Fly Ash	Clinton	Louisa	Neal 4	Council Bluffs	Ottumwa
0	0.06*	0.06*	0.06*	0.06*	0.06*
7.5	0.06	0.06	0.07	0.05	0.05
15	0.06	0.06	0.07	0.06	0.07
22.5	0.07	0.06	0.06	0.06	0.08
35	0.07	0.07	0.06	0.07	0.07
50	0.06	0.09	0.06	0.08	0.09
DAV cement (0.76% equivalent sodium oxide)					
% Fly Ash	Clinton	Louisa	Neal 4	Council Bluffs	Ottumwa
0	0.07**	0.07**	0.07**	0.07**	0.07**
7.5	0.05	0.08	0.09	0.07	0.07
15	0.05	0.08	0.08	0.08	0.09
22.5	0.07	0.07	0.08	0.07	0.09
35	0.06	0.08	0.08	0.09	0.09
50	0.06	0.10	0.08	0.09	0.09

\* based on n=4 and  $0.056 \pm 0.005$

\*\* based on n=4 and  $0.065 \pm 0.006$

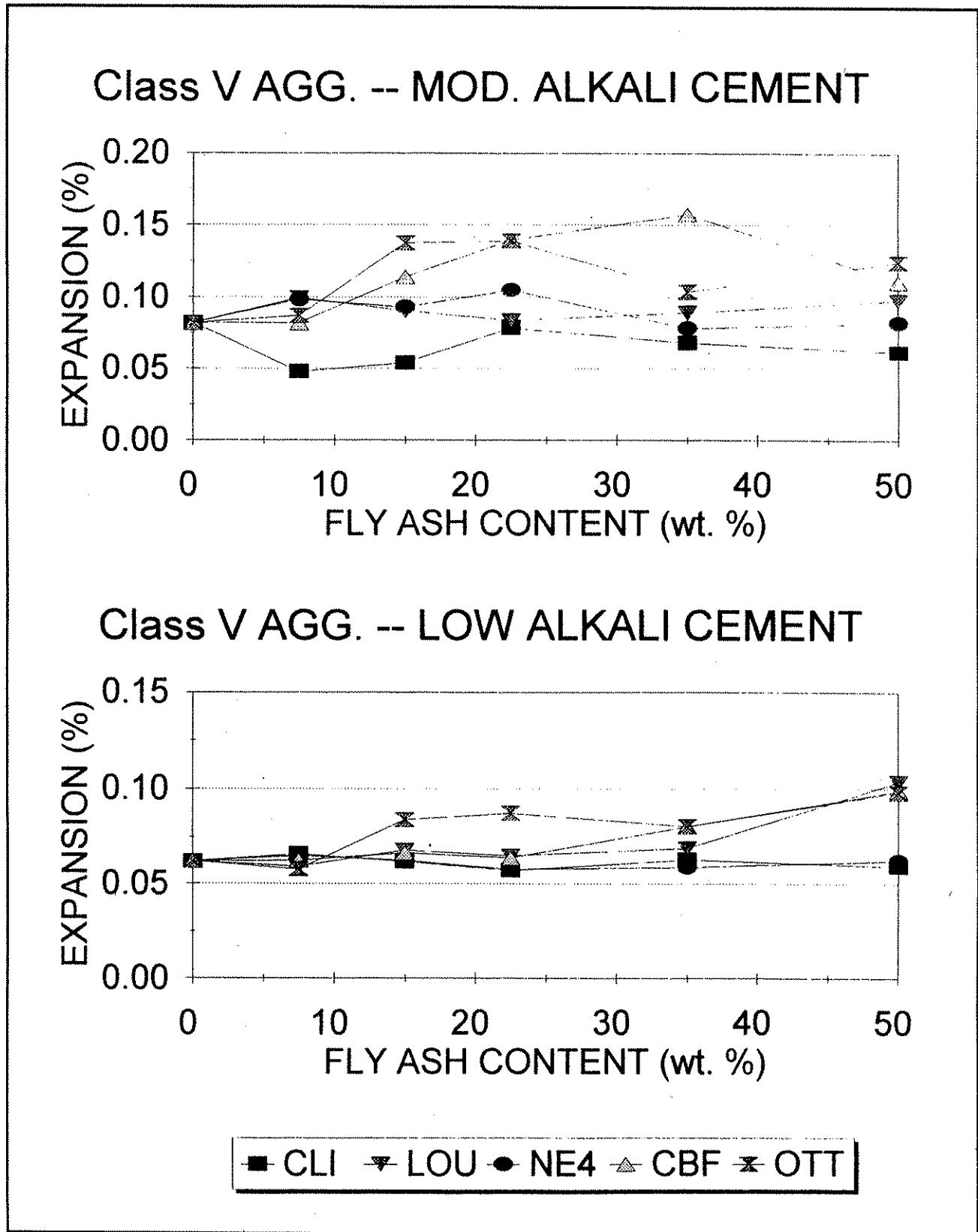
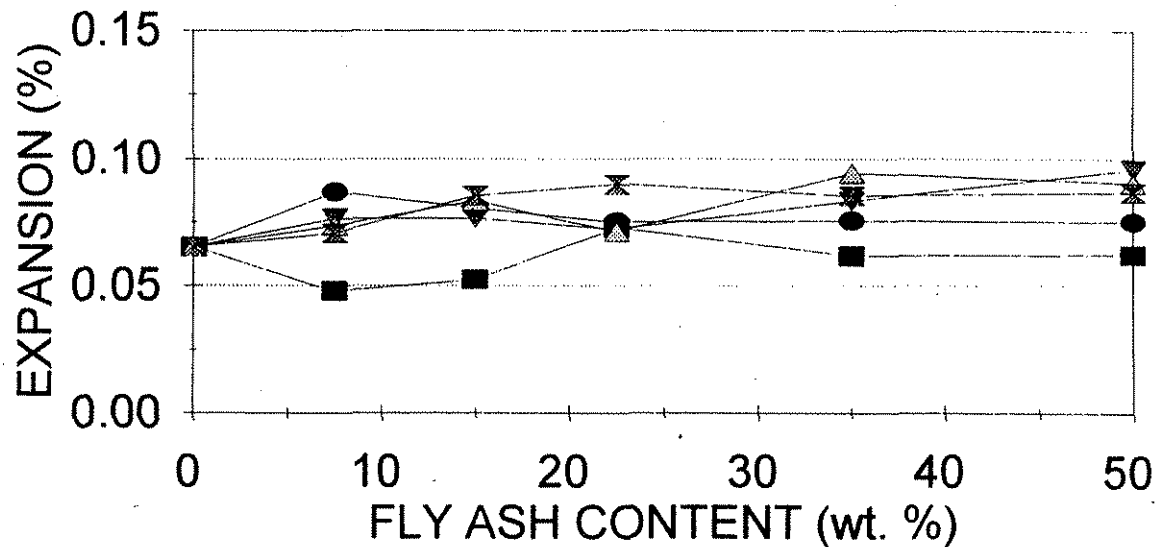
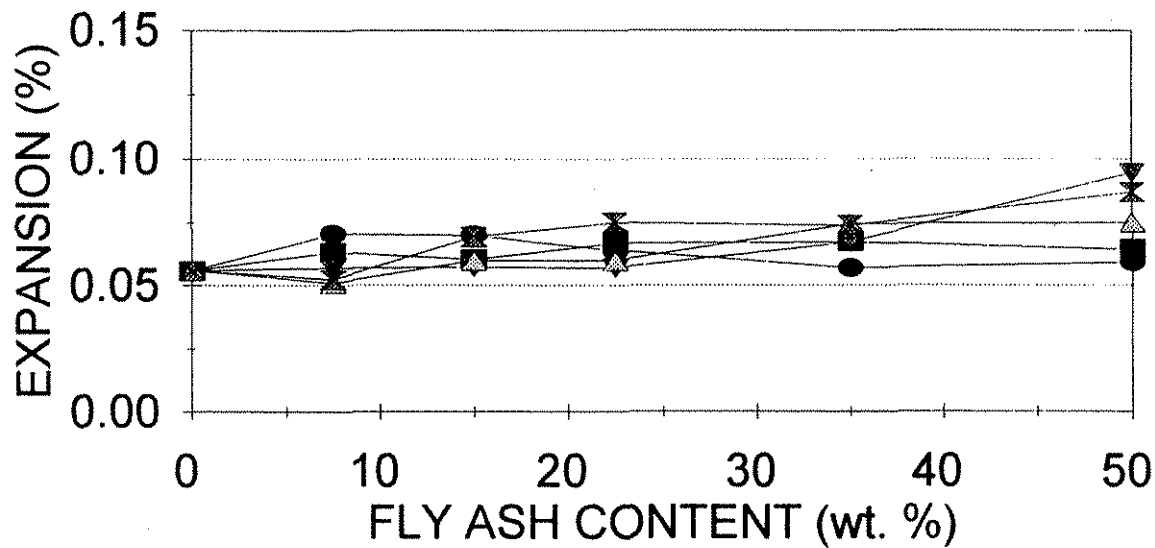


Figure 26. Expansion versus fly ash replacement for the specimens containing Class V aggregate.

### STD. SAND -- MOD. ALKALI CEMENT



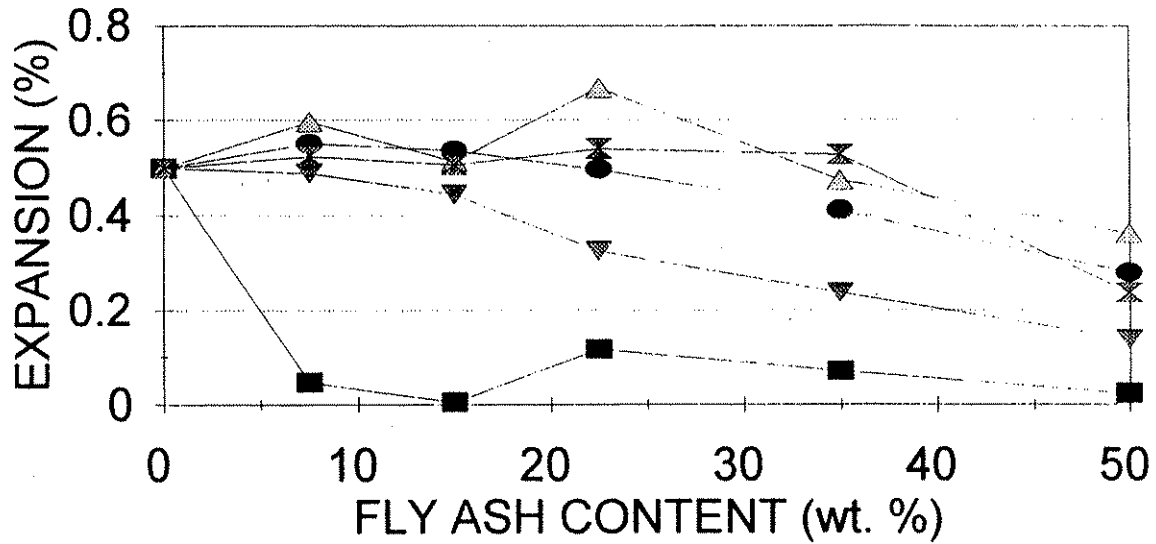
### STD. SAND -- LOW ALKALI CEMENT



■ CLI ▼ LOU ● NE4 ▲ CBF ✕ OTT

Figure 27. Expansion vs. fly ash replacement for specimens containing standard sand aggregate.

## PYREX GLASS -- MOD. ALKALI CEMENT



## PYREX GLASS -- LOW ALKALI CEMENT

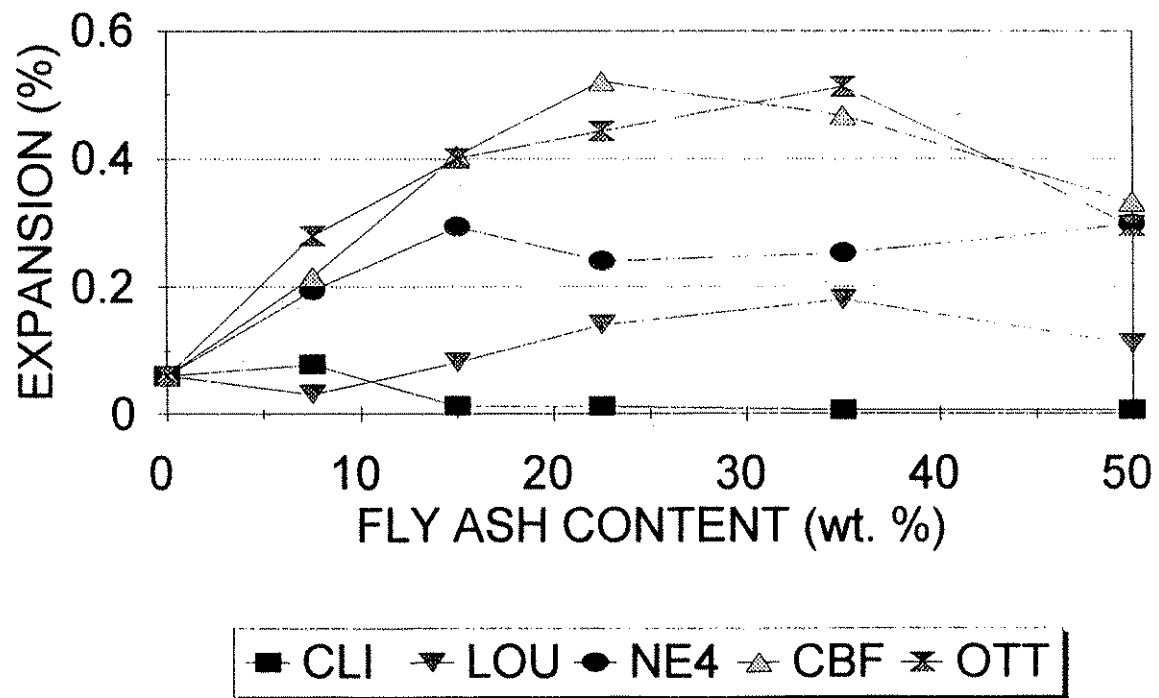


Figure 28. Expansion versus fly ash content for the specimens containing Pyrex glass aggregate.

Figure 26 depicts the test results that were obtained when using the Class V aggregate. All the values plotted in the figure were taken from Table 21; and hence, were the expansion values that were measured at 21 months of curing. This particular aggregate does tend to show some expansive behavior when used in combination with the moderate alkali cement and either Ottumwa or Council Bluffs fly ashes. The failure criteria suggested by the ASTM for this test method are 0.02 percent expansion at 14 days, 0.05 percent expansion at 3 months and 0.10 percent expansion at 6 months [3]; hence, there is no direct limit stated that can be applied to these test results (i.e., measured at 21 months). These same test specimens met the ASTM expansion requirements at 14 days, 3 months and 6 months. The test specimens that contained the low alkali cement did not expand as much as the specimens that contained the moderate alkali cement.

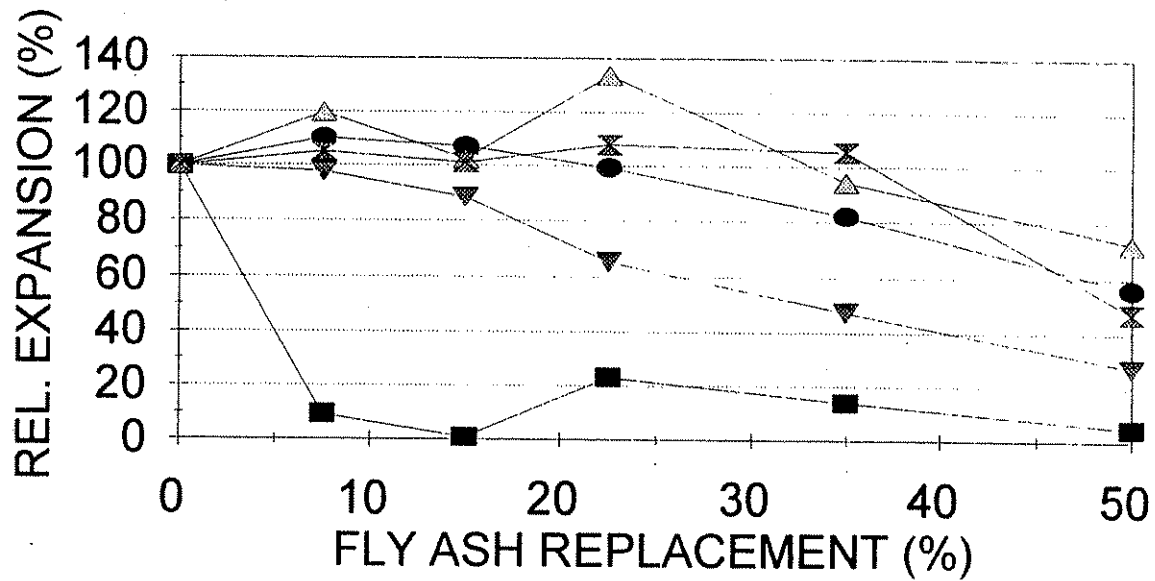
Figure 27 depicts the test results that were obtained from the specimens containing the standard sand as an aggregate. This series of mixtures were originally made to produce a "bland" or "background" measurement that could be used to assess the expansive potential of the other two sources of aggregate. However, as is evident in Figure 27, the test specimens containing the standard sand aggregate also exhibited a measurable response to the test procedure. The "background" expansion of the test specimens was about 0.06 percent at 21 months. This expansion did not appear to be significantly influenced by the alkali content of the two cements that were used in the study. However, the test specimens that contained Louisa, Ottumwa or Council Bluffs fly ash tended to exhibit trends of increasing expansion with increasing fly ash replacement. This trend was also observed in the specimens made with the Class V aggregate (it is most evident in the mortar base containing the low alkali cement). The remaining two fly ashes (Neal 4 and Clinton) did not exhibit this type of behavior and produce nearly flat expansion versus fly ash content curves. This suggests that we may be observing specimen expansion that is not related to ASR. Such a phenomenon has already been suggested by Johnston [31], who related the expansion to bulk MgO content. Our data, which refers to measurements taken at 21 months, indicates that the effect may increase the specimen expansion by about 0.03 to 0.04 percent by the time that you reach 50 percent fly ash replacement. Hence, these effects are quite small but they are certainly measurable, and, as was the

case in this particular instance, they may make a significant contribution to the overall test response. Our test measurements were too imprecise to attempt a reliable correlation study but it is interesting to note that the three fly ashes with the highest periclase (MgO) contents (see the diffractograms in Appendix A) consistently exhibited this type of behavior.

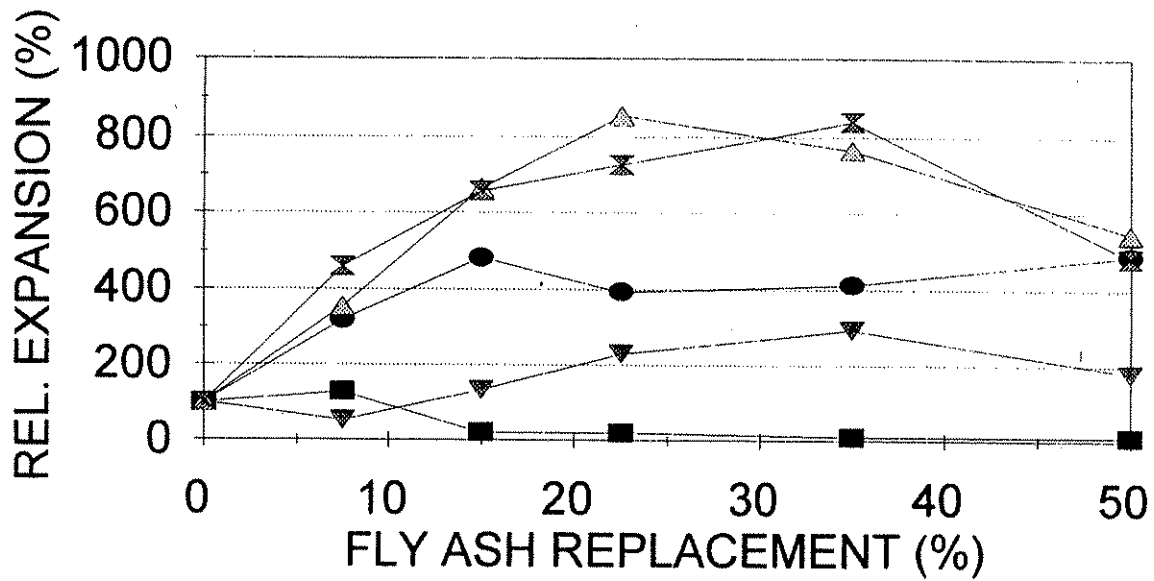
Figure 28 depicts a "worst case" scenario because the mortar bars were made with an extremely alkali-reactive aggregate (crushed Pyrex glass). All of the fly ashes exhibited a "pesimum" percentage of fly ash replacement in the mixes containing the low alkali cement. This percentage was normally in the range of about 15 to 35 percent replacement. However, this same trend was not always evident in the mixes containing the moderate alkali cement. Hence, one can conclude that the fly ashes did contribute a significant portion of alkalis to the pore solutions of the mortars but that their influence is much greater when using low alkali cements than when using cements with moderate (0.75 percent) alkali contents. This trend is much more apparent when the expansion data is transformed from an absolute basis to a relative basis (i.e., expansion of the portland cement control specimens = 100 percent). This information is depicted in Figure 29. The upper half of Figure 29 indicates that only one set of test specimens that were made with the moderate alkali cement exceeded a relative expansion value of 120 percent (i.e., an increase in expansion of 20 percent). In contrast, the bottom half of Figure 29 indicates that when the same fly ashes were used with the low alkali cement nearly all of the specimens exceeded a relative expansion value of 200 percent. Only the Clinton fly ash and low percentages of the Louisa fly ash were able to reduce the expansion of the test specimens below the value that was observed for the low alkali control specimens.

The performance of the different fly ashes with the Pyrex glass aggregate is difficult to explain using an explanation based only on the alkali content of the fly ashes. Even when the cement alkalis are included in the calculations it is difficult to explain why the Council Bluffs fly ash often performs the same or even worse than the Ottumwa fly ash. Also, why did the Louisa and Neal 4 fly ashes, which have very similar chemical compositions, behave so differently in the Pyrex ASR study? And finally, why did the Class C fly ashes exhibit such broad pessimum curves? Perhaps a

# PYREX AGG. - MOD. ALKALI CEMENT



# PYREX AGG. - LOW ALKALI CEMENT



■ CLI ▾ LOU ● NE4 ▲ CBF ✕ OTT

Figure 29. Relative expansion vs. fly ash content for specimens containing Pyrex glass aggregate.



partial explanation for these various questions can be attributed to the presence of cristobalite (or a glass phase similar to cristobalite) in three of the Class C fly ashes (Neal 4, Ottumwa and Council Bluffs). The concentration of cristobalite in these three fly ashes is rather small, probably only a few percent, and its particle size is not known. Hence, one must question if such a material will behave as a pozzolan (small particle size) or an aggregate (large particle size), but in either case the cristobalite should produce alkali-silica gel. Due to the low concentration of cristobalite in the fly ashes, it will take large fly ash replacements to push the cristobalite content of a test specimen over the pessimum proportion. When relative performance ratings are assigned to the test specimens (based on the graphical information in Figures 28 or 29) it is apparent that the cristobalite concentration places the fly ashes in the proper order (see Table 22).

**Table 22. Performance (negative basis) of the various fly ashes in the Pyrex glass study.**

Performance	Fly Ash	Available Alkali (% equiv. Na <sub>2</sub> O @ 28 days)	Available Alkali (% equiv. Na <sub>2</sub> O @ 145 days)	Cristobalite (Net intensity, counts)	Oxide Sum (SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub> )
1 (Best)	Clinton	0.91	0.9	0	84
2	Louisa	1.28	1.6	0	64
3	Neal 4	0.94	1.4	500	59
4	Ottumwa	1.94	2.2	1700	57
5 (Worst)	Council Bluffs	1.65	1.85	3180	55

The Iowa DOT has already conducted several studies to identify the alkali-sensitive aggregates that are present in Iowa. The first study was conducted by Moussalli and Riley and reported in 1980 [33]. The purpose of this study was to evaluate how increasing cement alkali contents would impact the integrity of concrete pavements and structures in Iowa. The study investigated the alkali-reactivity of 31 different aggregates using the quick chemical test (ASTM C 289) and the mortar bar method (ASTM C 227). The results of the study indicated that none of 31 aggregates that were tested could be definitely (conclusively) identified as alkali-sensitive.

The second study was conducted by Jones and reported in 1989 [34]. The objectives of the study were to: {1} test the effectiveness of the new ASTM C 227 test containers; and {2} to study the effect of three Iowa fly ashes on the alkali-silica reaction. Three different cements (high, low and very low alkali), three different aggregates (Pyrex glass, Oreapolis and Cordova) and three different fly ashes (Louisa, Ottumwa and Council Bluffs) were used in the study. The test results indicated that neither the Oreapolis or Cordova aggregates exhibited an alkali-silica reaction problem (although the Cordova aggregate did tend to perform slightly better than the Oreapolis aggregate). However, Jones also expressed his concern about the expansive tendencies that were observed when the Class C fly ashes were used in the mortar bar specimens. This behavior was most obvious in test specimens that contained the Pyrex glass aggregate in combination with the Council Bluffs fly ash and the low alkali cements, or test specimens that contained the Oreapolis aggregate in combination with any of the fly ashes and the high alkali cement. Few trends could be discerned in the specimens that contained the Cordova aggregate. Hence Jones recommended that the Class C fly ashes should be included in future testing programs.

Recently the Iowa DOT has turned to a new test method (ASTM P-214 to evaluate the alkali-reactivity of a wide variety of Iowa sands. Preliminary results of this study have suggested that many of the sands are alkali-sensitive [35]. In fact, of the thirty sources of sand that were evaluated, only two sources were classified as innocuous. Seventeen of the sands produced in conclusive test results and the remaining eleven sources were classified as reactive. The Oreapolis sand was classified as alkali-reactive and it produced the fourth largest test response (expansion) that was observed for the thirty different sands that were studied. Hence, we have learned a great deal about the reactivity of Iowa sands since the early studies were conducted. Obviously, as was pointed out by Jones [34], the early alkali-reactivity studies were plagued by experimental difficulties (i.e., shrinkage rather than expansion) and the accuracy of their test results must be questioned. However, how can the difference between the study by Jones (Oreapolis non-reactive) and the new P-214 study (Oreapolis reactive) be resolved?

The test results that have been presented in this research report have verified those that were

reported by Jones in 1989. In fact, this study includes observations that span a period of 21 months (instead of the six month period used by Jones). After 21 months at 38° C, the test specimens that contained the moderate alkali cement and the Oreapolis aggregate still did not exceed the six month expansion criterion of 0.1 percent. Several of the test specimens containing Class C fly ashes (Council Bluffs, Ottumwa and Neal 4) did exceed the 0.1 percent expansion criterion; however, this study has identified two additional factors that influence expansion, namely periclase content and cristobalite content.

## SUMMARY AND CONCLUSIONS

In summary, a detailed investigation has been made to assess how Iowa fly ashes influenced the chemical durability of portland cement based products. This study was conducted to provide a sound empirical database which can be used to predict how deicer salts that contain sulfate impurities affect the integrity of Iowa pavements.

Sulfate durability tests were conducted on portland cement-fly ash pastes, mortars and concretes. The mortar bar tests were conducted using a procedure similar to that described in ASTM C 1012. The concrete tests were conducted using a procedure similar to that used by the U.S. Bureau of Reclamation. Both studies investigated sulfate soak solutions and synthetic deicer soak solutions. Several additional mortar studies were conducted to evaluate how the mortar bar studies were influenced by the concentration of the sulfate and chloride solutions and the duration of curing before immersion in the sulfate soak solutions.

Alkali-aggregate reactivity tests were conducted to assess how Iowa fly ashes influenced the expansion of ASTM C 311 mortar bar specimens.

The results of this research effort, and the conclusions that have been made by careful interpretation of these test results, can be summarized as follows.

1. The results of the ASTM C 1012 mortar bar studies (5 percent sodium sulfate soak test) indicated that:

- Sulfate resistance of the control mortar specimens tended to increase with decreasing content of tricalcium aluminate ( $C_3A$  content calculated via ASTM C 150).
- Sulfate resistance of test specimens containing Clinton or Louisa fly ashes tended to increase with increasing fly ash replacement. This trend was consistent regardless which type of cement was used in the test specimens. In fact, test specimens containing thirty percent Clinton or Louisa fly ash easily outperformed the Type V control specimens.
- Sulfate resistance of the test specimens containing Ottumwa or Neal 4 fly ashes was neither increased nor decreased relative to the appropriate control specimens.
- Sulfate resistance of the test specimens containing the Council Bluffs fly ash was decreased with respect to the appropriate control specimens.
- Sulfoaluminate corrosion was identified as the major failure mode for the mortar bar specimens. Most of the test specimens exhibited expansive tendencies that were relatively uniform throughout the mortar bar, with little evidence of surface spalling or corner breakage.

2. The results of the mortar bar specimens that were subjected to the synthetic deicer soak solution (9.5 percent  $NaCl$  + 0.25 percent  $Na_2SO_4$ ) indicated that:

- All of the fly ashes tended to increase the sulfate durability of the test specimens that were made with the Type I portland cement. Typically, sulfate durability increased with increasing fly ash replacement.
- Many of the fly ashes (Clinton, Louisa and Neal 4) tended to increase the sulfate resistance of test specimens that were made with the Type I-II portland cement. The remaining two fly ashes (Ottumwa and Council Bluffs) had to be used at replacement levels above 15 percent to improve the sulfate resistance of the test specimens.
- All of the fly ashes except the Clinton ash reduced the sulfate resistance of the test specimens that were made with the Type V portland cement.
- Sulfoaluminate corrosion was identified as the major failure for the test specimens that were subjected to the synthetic deicer soak test. However, the improved sulfate resistance of the specimens containing Council Bluffs fly ash and Type I portland cement was attributed to the formation of Friedel's salt rather than monosulfoaluminate. Friedel's salt did not appear to be expansive in the synthetic deicer solution.

3. The results of the curing study that was conducted on the mortar bar specimens indicated that:

- Compressive strength had little influence on the results of the sulfate durability tests. Instead, it appeared that porosity and specimen chemistry tended to dominate the sulfate resistance of the test specimens.

4. The results of the concentration study that was conducted on the mortar bar specimens indicated that:

- Specimen distress and time to failure can be drastically altered by altering the concentration of the sulfates in the test solution. Typically, test specimens failed more rapidly in test solutions that contained higher concentrations of sulfates.

5. The results of the paste study (5 percent sulfate soak test) indicated that:

- Test specimens containing Council Bluffs fly ash and Type I cement failed very slowly compared to the mortar bar test specimens. This suggests that specimen porosity may dominate the failure mechanism (sulfoaluminate corrosion) at low water/cement ratios.
- Scanning electron microscopy studies indicated the presence of diffusion rims in the test specimens. The rims tended to be enriched in sulfur when compared to the interior of the test specimen. This was in agreement with the failure mode exhibited by many of the specimens, which indicated that the specimens tended to spall off edges and corners.

6. The results of the concrete study indicated that:

- The expansion rate of the concrete test specimens was very slow. In fact, at the time of writing this report, none of the concrete specimens had yet reached the 0.1 percent failure criterion. If this criterion was reduced to 0.05 percent expansion, only the Type I control concrete specimens would have failed the test.
- Relative dynamic modulus readings and weight measurements were consistent with the expansion measurements. Hence, all three measurements indicated that the concrete test specimens were in a reasonably sound condition.
- Visual inspection of the test specimens indicated a failure mode that was due to surface spalling at edges and corners. Typically, visual inspection suggested that sulfate resistance increased with increasing fly ash replacement (30 percent maximum replacement). Clinton fly ash appeared to perform the best; however, the four Class C fly ashes also appeared to be performing reasonably well.

- Based on U.S. Bureau of Reclamation sulfate durability studies, which have indicated that one year of laboratory exposure (10 percent soak test) is equivalent to about six years of service life, the concrete mixes summarized in this report have endured:

Jabens aggregate (116 weeks exposure)	≅ 13 years service life
Lamont aggregate (104 weeks exposure)	≅ 12 years service life
Montour aggregate (64 weeks exposure)	≅ 7 years service life
Early Chapel aggregate (52 weeks exposure)	≅ 6 years service life

Since none of the concrete test specimens were on the brink of failure, one may conclude that the Iowa DOT C-3 concrete mixes exhibit good resistance to sulfate attack. The information listed in this report indicates that the failure due to sulfate attack should be slow (not catastrophic) and that in properly constructed projects the attack should be controlled by the permeability of the concrete (i.e., failure should progress from the outside (exposed side) to the inside of the member; corners and edges being the first indicators of sulfate induced degradation.

- Concrete test specimens that were placed in the synthetic deicer soak solution have exhibited only minor deterioration over the course of this study. These test specimens have expanded about the same magnitude as the test specimens that were placed in the 10 percent sodium sulfate solution; however, a visual assessment of the various test specimens has yielded little evidence of surface spalling or corner breakage. Hence, the synthetic deicer soak specimens appear to be failing at a very slow rate.

7. The results of the alkali-reactivity mortar bar tests have indicated that:

- The Oreapolis aggregate is not very sensitive to alkali-aggregate reaction. This experimental program has verified both the observations and conclusions reported in an earlier study conducted by Jones. The duration of the present study has exceeded 21 months of exposure to the test conditions and the measured expansions of the control test specimens were all less than 0.1 percent (the six month criterion set by the ASTM). This conclusion is based on the use of a moderate alkali cement (0.8 percent equivalent sodium oxide); however, the study by Jones incorporated a high-alkali cement and he reported identical conclusions.
- Two additional factors have been identified that appear to influence the mortar bar test results. These two additional factors appear to be most commonly found in Class C (high-calcium) fly ashes. First, the periclase (MgO) content of the test specimens increases the expansion of test specimens at high (above 30 percent) fly ash replacements. Secondly, several of the Class C fly ashes contain a poorly crystalline material similar to cristobalite, and this tends to cause poor performance in the mortar bar tests. Obviously, these two factors act in unison with the alkalis released by the fly ash to cause expansion in the mortar bar specimens. These additional two factors tend to complicate the interpretation of the mortar bar test results, especially when the test response (expansion) is small.

- All of the Class C fly ashes that were used in this study released large amounts of alkalis (primarily sodium) into the pore solution of the test specimens. This study indicated that the majority of the fly ash alkalis were released during the first two to three months of exposure to the test conditions. The single Class F ash that was used in this study also released alkalis (primarily potassium) into the pore solution but this release was nearly complete after about one month. Hence, the ASTM C 311 available alkali test only gives a reliable estimate of the alkalis that can be released from the Clinton (Class F) fly ash, it substantially underestimates the amount of alkalis that can be released from the Class C fly ashes.
- No simple relationship was found between fly ash alkali content and mortar bar expansion. In fact, several anomalies were noted that tend to suggest that such a relationship may not be valid for a system as complex as Class C fly ash-portland cement mortars.
- Clinton fly ash mitigated the alkali-silica reaction in nearly all of the test specimens that it was used in. In fact, it was the only fly ash that consistently reduced the expansion of test specimens that contained the Pyrex glass aggregate. The alkali content of the cement had only a small influence on the expansion of test specimens that contained Clinton fly ash.
- The four Class C fly ashes that were used in this study all performed in a similar fashion.

When the fly ashes were used with the very low alkali cement the alkalis from the fly ashes tended to dominate the expansion of the mortar bar specimens, this tended to produce broad pessimum curves in the test specimens containing the Pyrex glass aggregate. Few significant trends were evident in specimens containing the other two types of aggregates.

When the fly ashes were used with the moderate alkali cement the cement alkalis appeared to dominate the expansion of the mortar bar specimens containing the Pyrex glass aggregate. However, the specimens containing the Oreapolis aggregate appeared to be sensitive to the use of either the Council Bluffs or the Ottumwa fly ashes.

## RECOMMENDATIONS

Based on the experimental findings reported or discussed in this document, the following recommendations can be made.

1. A chemical testing program should be conducted on the various road salts that are commonly used in the state. The testing program should be constructed to provide information on a quality control basis.

2. A more conservative estimate of the alkali content of fly ashes should be adopted to replace the current "available alkali" test described in ASTM C 311. The available alkali test tends to underestimate the amount of fly ash alkalis that can be released into solution.
3. The concrete test specimens that are currently immersed in sulfate bearing solutions should be monitored until they reach failure. This would provide a better estimate of the service life of field concrete mixes containing Type I portland cements and various sources of fly ash.

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Iowa Southern Utilities  
Iowa Electric Light and Power Company  
Ames Municipal Electric System  
Interstate Power Company  
Iowa-Illinois Gas & Electric Company



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