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AVAILABLE ALKALIS IN FLY ASH AND THEIR EFFECTS ON ALKALI-
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Available alkalis in fly ash and

their effects on alkali-aggregate reaction

by

Chau Lee

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Since 1940, it has been known that the aggregate in concrete is not inert. Stanton [127, 128] reported that a deleteriously expansive reaction or so called alkali-aggregate reaction resulted from the interaction between alkalis (sodium and potassium) released from cement hydration and certain rocks and minerals occasionally present in aggregate used in concrete. The reaction may lead to local volume expansion, cracking, pop-out, loss of strength, dislocation structures, efflorescence problems in the finished product, and in extreme cases, to complete destruction of the concretes. Evidence of alkali-aggregate reaction has been found in many states in the United States (notably California, Oregon, Idaho, Arizona, Nebraska, New Mexico, Kansas, Virginia, Washington, and Wyoming) [94] and in many other countries in the world such as Australia [1], Canada [55], Denmark [18], Germany [5], Iceland [57], New Zealand [79], and South Africa [110]. Hence, much of the last 40 years has been spent researching these alkali related problems and defining specifications to minimize these problems.

It is obvious that alkali-aggregate reaction can be prevented by limiting the alkali content in cement or by using non-reactive aggregate in concrete. However, upon consideration of environmental protection and energy

efficiency, the newly developed dry-process kilns involve multistage gas suspension preheaters and move toward recycling a greater portion of alkali-rich dust to the kiln feed which offers little chance for removal of alkalis from the kilns. Hence, the alkali content of cement may be expected to increase continuously in the future. Also, in many areas the known high quality aggregates have become depleted, and the use of questionable or marginal aggregates is increasingly necessary for concrete construction. Alternatively, the addition of fly ash or other pozzolans as a mineral admixture to concrete has been commonly used to increase the concrete's resistance to alkali attack. However, problems may arise from this solution because all pozzolans do not exhibit equivalent reactivity with cement alkalis and also, the pozzolans themselves can significantly contribute to the alkali content of the pore solution in concrete [52, 24].

Fly ash is a widely available byproduct derived from combustion of pulverized ground coal, transported from the combustion firebox through the boiler by the flue gases into precipitators. Fly ash is rapidly becoming one of the most frequently used pozzolans because utilization of fly ash, instead of dumping it as a waste material, has economical, technological, and energy-saving advantages. The alkali content of fly ash can vary considerably since it is

influenced by many variables such as the composition of the coal, the rate and efficiency of combustion, the type of boiler and collection systems, and the pretreatment of raw coal with additives to enhance electrostatic precipitator performance.

The current trend towards increasing fly ash usage in construction projects has many advantages. But its usage also gives rise to future problems since the behavior of alkalis in fly ash and their effects on alkali-aggregate reaction in concrete are not fully understood. Therefore, basic research which would result in preventing deleterious alkali-aggregate reaction in fly ash concrete would be worthwhile.

Scope and Objective

The first section of this thesis deals with the available alkalis in fly ash. The measurement of available alkali content in fly ash is currently specified by the American Society for Testing and Materials (ASTM) as a standard method (C 311) [2]. There are several types or classes of pozzolans recognized by ASTM C 618 but only two of them, Class C and F fly ash, are to be considered in this study. The objectives of this section are: (1) to assess the significance of the test when it is used to analyze different fly ashes and (2) to investigate the possibility

of decreasing the time required to complete the test (it currently requires 28 days for curing).

The second section of this thesis deals with the effects of the addition of class C fly ash to concrete on resistance to alkali attack. ASTM C 441 gives a standard test method for effectiveness of mineral admixtures in preventing excessive expansion of concrete due to the alkali-aggregate reaction. Based on the types of aggregate, Gillott [48] classified the alkali-aggregate reactions into three categories: alkali-silica reaction, alkali-silicate reaction, and alkali-carbonate reaction. The term "alkali-aggregate reaction" used in this thesis implies mainly the alkali-silica and alkali-silicate reactions. The objective of this section is two-fold. First, the the significance of the standard test for different replacement percentages of both high and low-alkali cements by Class C fly ashes with different levels of alkali content (currently ASTM specifies a 25 percent replacement by volume of cement) will be evaluated. Second, the ability of Class C fly ash to improve concrete's resistance to alkali attack by alkalis from external sources such as de-icing salt and sea water will be investigated.

BACKGROUND AND LITERATURE REVIEW

Diagnosis of Alkali-Aggregate Reaction

The damage caused by the alkali-aggregate reaction can be assessed both in the field and in the laboratory by investigation of external and internal symptoms resulting from the reaction. The most apparent external symptom is the development of randomly distributed cracking, often referred to as map cracking, on the unrestrained concrete surface where moisture is most readily available [38, 42, 48, 49, 147].

In addition to the typical map cracking, the concrete surface may exhibit modified crack patterns due to concrete geometry, reinforcement, and restraints [12, 58, 64, 149]. Cracks tend to align themselves parallel to the direction of reinforcement or major principal stress in the concrete, or along the length of a concrete column or beam. Affected concrete may also show pop-outs above large reactive aggregates close to the concrete surface [48, 49, 58, 64, 147]. The other external symptom is the exuding of the reaction products from cracks at the concrete surface. These can take the form of a watery gel, a viscous drop, or a wet spot [42, 48]. The exuded gel reacts with carbon dioxide and dries to form a white deposit. The absence of a reaction product on the concrete surface does not imply that

no damage is caused by the reaction because the reaction product may be cleaned by surface erosion or washing [49, 147].

Cracks, pop-outs, and various exudates may originate from causes other than the alkali-aggregate reaction, such as freeze-thaw cycling, drying and wetting, or sulphate attack. To make sure the damage is caused by the alkali-aggregate reaction, it is recommended that the internal symptoms in the spalled concrete be examined microscopically, These symptoms include microcracks, gel like reaction products, and dark rim around the reacted aggregates. Microcracks are present within the aggregate surface, sometimes link voids, and sometimes extend into cement paste. In the cement matrix, microcracks may propagate from positions where concentrated stress is produced such as corners of angular aggregates; some cracks may be followed from aggregate to aggregate [10, 41]. The reaction product which is colorless and transparent or white and porcelaneous in the form of a gel or sol can be frequently found in cracks or voids within concrete [48, 94]. The occurrence of dark rims surrounding reacted aggregate particles indicates the zone of reaction, but it should be noted that weather or other natural forces may also result in dark rims for aggregates [49, 94, 147].

Mechanism and Chemistry of Alkali-Aggregate Reaction

The simplified sequential processes of alkali-aggregate reaction involve: (1) penetration of hydroxyl and alkali ions present in concrete pore solution into the interior of poorly crystalline silica, (2) rupture of Si-O-Si bonds through hydroxyl attack, (3) balance of negative charges resulting from hydroxyl attack by diffusion of alkali cations, (4) partial substitution of alkali ions by calcium ions to form reaction products such as alkali-silicate gel or lime-alkali-silicate gel, and (5) imbibition of water by reaction products to produce expansive pressure causing concrete damage. The alkali-aggregate reaction processes of are summarized in Figure 1. Ideas concerning reactive aggregates, pore solution in concrete, reaction chemistry, migration of ions, and reaction products are reviewed in the following paragraphs.

Reactive Aggregates

Gillott [48] subdivided the alkali-aggregate reaction according to the type of aggregates, namely, alkali-silica reaction, alkali-silicate reaction, and alkali-carbonate reaction. The aggregate in the alkali-silica reaction category involves mainly: (1) poorly-crystalline or hydrous silica materials such as opal, chert, and flint; (2) glassy to cryptocrystalline aggregates such as rhyolite, andesite,
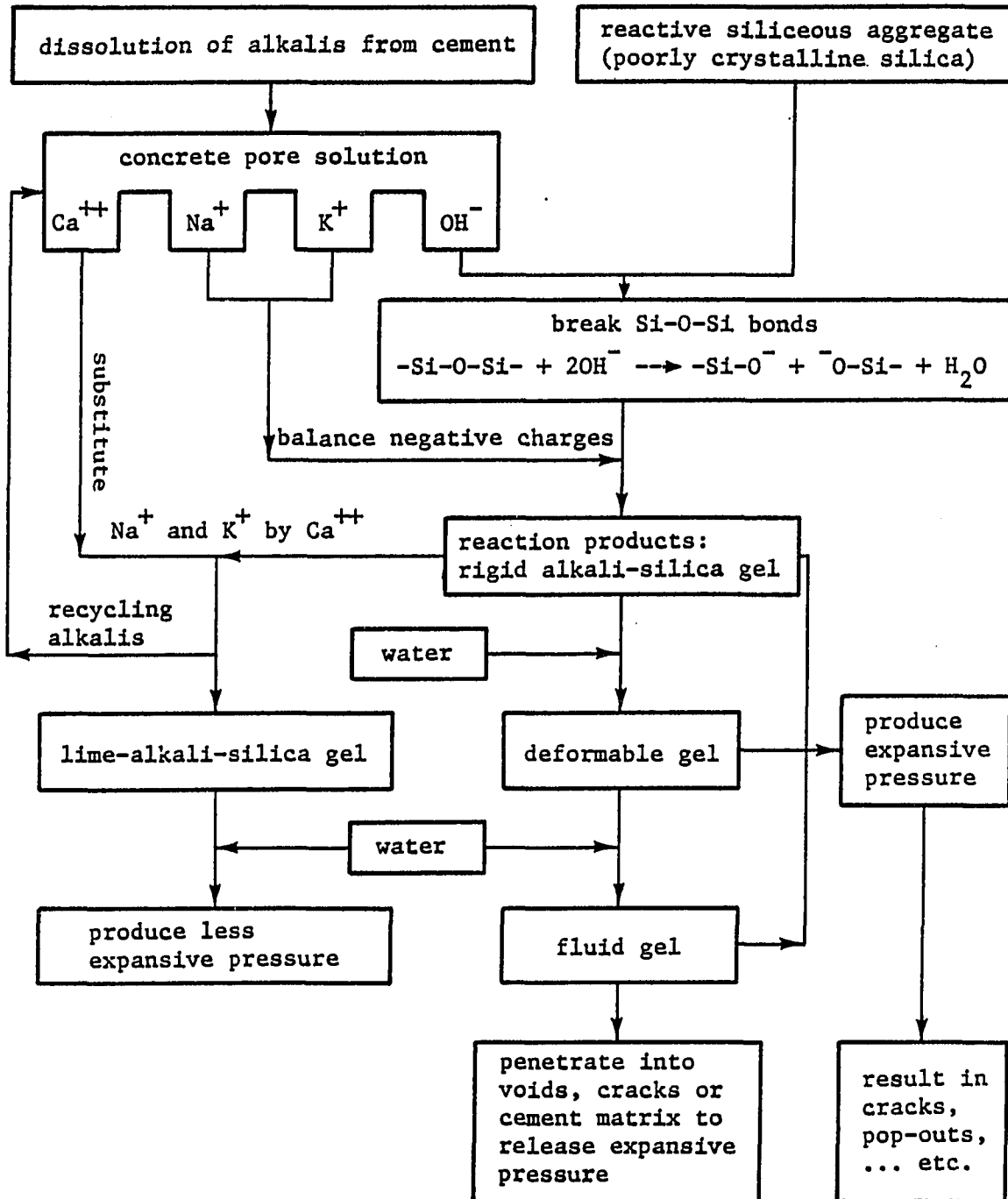
FIGURE 1. Schematic alkali-aggregate reaction processes

dacites, latites and artificial glasses; (3) microcrystalline and cryptocrystalline forms of quartz; (4) quartz crystals that are intensely fractured or strained; (5) cristobalite; and (6) tredymite [62]. The alkali-silicate reaction involve argillaceous and dolomitic limestones, phyllites, greywackes, argillites, and some granitic rocks. The aggregates producing alkali-carbonate reactions are not included. Diamond [29] has also made a review of siliceous reactive aggregates.

Aggregates are alkali reactive because of their poorly-crystalline and open structure, relatively low density and silicon-oxygen bond defects. The reactivity of siliceous. aggregates depends on the morphology and degree of disorder of their lattice structures [42]. Hydrous forms of silica such as opal, chalcedony or cristobalite are particularly reactive, highly strained quartz and microcrystalline forms of quartz are slowly reactive at normal temperatures, and chert and flint exhibit variable reactivity. Though the reaction rates of silica-bearing aggregates with alkalis are variable, the basic reaction is due to rupture of O-Si-O bonds through reactions with the alkaline pore solution in the cement paste [62]. Thus, the number of silicon-oxygen bond defects in the reactive aggregate has a major effect in determining the reactivity and the rate of alkali-aggregate reaction.

Pore Solutions in Concrete

Barneyback and Diamond [6] developed a pore solution extraction device to study the compositions and concentrations of pore solution in hardened cement pastes or mortars by squeezing the solution out from the specimen under a pressure of 550 MPa (80.000 psi). After this device was developed, Diamond [27, 31], Diamond and Barneyback [32], and Diamond and Lopez-Flores [33] published their studies on concrete pore solutions, and concluded that these results were representative of pore solutions within pastes or mortars. The ions found in quantifiable amounts were alkali (sodium and potassium) and hydroxyl ions at relatively high concentrations, together with smaller concentrations of calcium and sulphate ions. Silicon, aluminum, and iron-bearing ions were not found in quantifiable amounts.

Alkali cations   Most of alkalis present in cement were found to be either in the form of alkali sulfate or in the form of solid solution with calcium silicate or aluminate. The alkalis in the form of sulfate were rapidly dissolved into the mixing water, and the dissolution of alkalis from the solid solution phase was greatly dependent upon the hydration rate of cement. Their studies indicated that more than 70 percent of alkalis in cement mobilize into the pore solution, and tend to persist in that state.

The alkali concentrations in the pore solution varied with the alkali content of the cement, the cement content in concrete, the amount of mixing water, the mobilization rate of cement alkalis, and the progress of cement hydration. According to their results, the behavior of alkali cations in pore solution can be summarized as follows:

1. The alkali concentration increases with time when isolated from additional water supply.

2. Some of the alkalis may be considerably delayed in reaching the pore solution.

3. Some of the alkali cations may enter solid solution within the cement hydration products.

4. Some of the alkali in the reaction products of alkali-silica reaction may be recycled by displacement of alkalis by calcium.

Sulfate and hydroxyl anions   Sulfate anion in the pore solution is initially found to be at a high concentration level followed by a decline due to formation of ettringite. According to Diamond [31], after the sulfate anion produced by added gypsum has been exhausted in precipitation of ettringite, further removal of sulfate anions from the pore solution will cause the hydroxyl anions generated by the cement hydration reactions to balance the positive charges of alkali cations remaining in the pore solution. Thus, generation of hydroxyl anions from alkali

sulfates seems to be delayed until the precipitation of
ettringite is essentially completed. For alkali cations
derived from solid solution, hydrolysis of anions will
directly yield hydroxyl anions. Though the concentration of
hydroxyl anions in pore solution is less than the combined
concentrations of the sodium and potassium cations during
the early stages of hydration, the hydroxyl anion
concentration is essentially equal to those of sodium plus
potassium at later stages. The pH value in the pore
solution of high alkali cement paste is frequently found to
be greater than 13.

Dent Glasser and Kataoka [22] have also proposed two
types of reactions to generate hydroxyl anions in pore
solution. These are:

1. Hydrolysis of anions of weak acids
   (e.g., silicates):

   $$X^{n-} + H_2O \longrightarrow HX^{(n-1)-} + OH^-$$
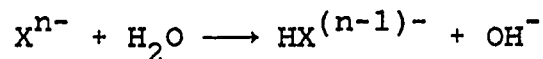
2. Formation of insoluble calcium salts
   (e.g., sulphate) rather than calcium
   hydroxide:

   $$2/n\ X^{n-} + Ca(OH)_2 \longrightarrow CaX_{2/n} + 2OH^-$$
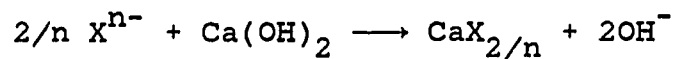
<u>Calcium cations</u>   Since the pore solution in cement
pastes is readily saturated or supersaturated with respect
to calcium hydroxide, the concentration of calcium ions is
initially on the order of 0.04 N which is the concentration
corresponding to pure saturated calcium hydroxide. This

concentration remains relatively stable for the first few hours, followed by a progressive decline toward a very low or even undetectable level attained after a long period of time [27, 28, 31, 46]. This reduction of calcium ion concentration may be attributed to the effect of the presence of alkali cations which depress the solubility of calcium hydroxide [136, 143].

Chemistry of alkali-aggregate reaction

The alkali-silica reaction is primarily caused by the attack of hydroxyl ions on the reactive siliceous aggregates rather than by the attack of alkali cations [27]. However, the hydroxyl ion content is greatly influenced by the alkali ion content. Vivian [144] added tetramethyl ammonium hydroxide, which can be strongly ionized in aqueous solution, to mortar containing opal and very low-alkali cement. He found the same symptoms as conventional alkali-silica reaction on the mortar surface. This suggests that attack on opal depended on the establishment of a high concentration of hydroxyl ions. Thus, the hydroxyl ion should be considered the reacting ion.

Dent Glasser and Kataoka [22] proposed diagrammatic models, as shown in Figure 2, to illustrate the difference in the attack process between well crystallized silica and poorly crystalline hydrous silica. Attack on well crystallized silica is a slow surface reaction producing

discrete silicate ions which are able to migrate away from
the reaction site into the fluid phase. In poorly
crystalline hydrous silica, hydroxide and alkali ions
penetrate into the interior of the aggregate to cause
disintegration of the network by rupture of Si-O-Si bonds
through hydroxyl attack producing an alkali-bearing cross-
linked polyelectrolyte. An imbibition pressure may be set
up when this structure contacts water because the silicon-
oxygen framework is partly disrupted.

According to Powers and Steinour [116], and Dent
Glasser and Kataoka [22, 24], two reactions might occur when
silica such as opal or flint was placed in sodium hydroxide
solution. According to these authors, initially, an acid-
base reaction takes place, in which silanol groups (Si-OH)
on the silica surface react with hydroxyl ions of the
solution to form a free water molecule, leaving negatively
charged surface-oxygen atoms balanced by sodium ions that
simultaneously diffuse into the structure. This reaction
also occurs when a dilute sodium hydroxide and well-
crystallized or other dense forms of silica are used. The
attraction of positive ions such as alkali and calcium ions
is called the Donnan effect or ion exchange [63, 113, 137].
When the sodium hydroxide concentration is high enough, the
sodium hydroxide not only removes and neutralizes the
surface hydrogen ions, but also attacks the siloxane bridges

(a)

(b)

•	o	⊕	◐
Si	O	Na (or K)	OH
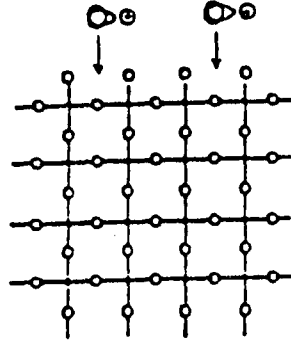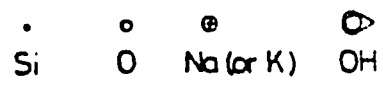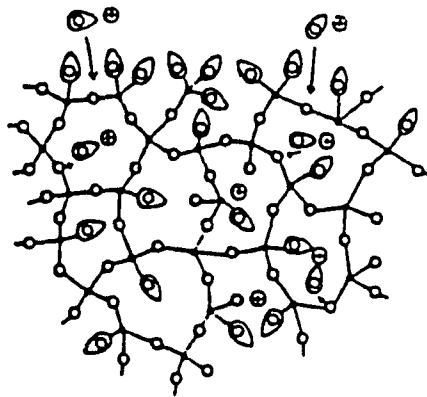
FIGURE 2. The attack of alkali on well crystallized silica
(a) and on poorly crystallized hydrous silica (b)
[22]

(Si-O-Si) as further hydroxyl ions diffuse into the structure.

$$-Si-O-Si- + 2NaOH \longrightarrow -Si-O^--Na^+ + Na^+-O^--Si- + H_2O$$
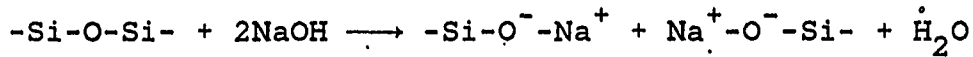
By this process, amorphous silica structure is loosened and its capacity to absorb sodium ions and water molecules is increased. Krogh [82] reported that the reaction rate depended on the amount of broken bonds in the silica lattice, on the available surface and on the hydroxyl ion concentration.

Dent Glasser and Kataoka [25] have also studied a model system for the alkali-aggregate reaction, placing solid silica gel in continuously stirred sodium/calcium hydroxide solutions. They suggested that four reactions might take place more or less simultaneously:

1. Silanol groups on the surface of the silica gel react with hydroxyl ions in the solution.

2. Sodium and calcium ions bind (through electrostatic attraction) at the negative charges thus created on the surface.

3. Silica gel dissolves through hydroxyl attack to give a solution whose silicon concentration depends both on pH and on the presence of ions such as calcium ions capable of forming insoluble silicates.

4. Silicate species in solution react with calcium ions to form C-S-H species.

Another simplified representation of the formation of alkali-silica gel has been reviewed by French [46] and Bakker [4] as follows:

$$SiO_2 \text{ (solid)} + NaOH_{(aq.)} \longrightarrow NaHSiO_3 \text{ (solid)}$$

and

$$NaHSiO_3 \text{ (solid)} + NaOH_{(aq.)} \xrightarrow{H_2O} Na_2SiO_3 \cdot xH_2O$$
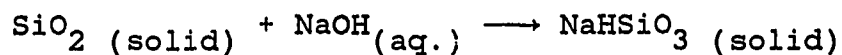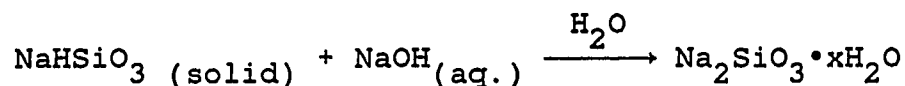
They postulated that the alkali-silica gel might react with the free lime released by hydration of cement to give an insoluble lime-alkali-silica gel with possible regeneration of part of the alkali. This reaction of recycling alkalis may be presented as:

$$Na_2SiO_3 \cdot xH_2O + Ca(OH)_2 \xrightarrow{H_2O} CaSiO_3 \cdot nH_2O + 2NaOH$$
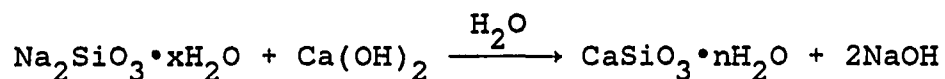
Migration of ions

Vivian [137] explained that the movement of alkali and hydroxyl ions during the reaction is due to diffusion caused by a concentration gradient. An hydroxyl concentration gradient is established because the hydroxyl ions disappear from the solution phase after reacting with opal. Positively charged alkali ions diffuse into the opal to maintain an electric balance, the Donnan effect, though the alkali concentration on the opal particle surface is equal

to or greater than that in the solution. The diffusion of ions continues until either the available alkalis or opal is exhausted.

Powers and Steinour [117] suggested that diffusion of ions or molecules through a gel containing a solution might take place in two ways: "(1) through the liquid phase in the ordinary way, and (2) by surface diffusion if soluble material is subjected to adsorption by the solid phase." Surface diffusion is a migration of adsorbed ions from one part of the internal surface to another part caused by surface concentration gradient. Furthermore, they gave their hypotheses for diffusion processes:

1. Diffusion of alkali from the surrounding concrete to the boundary of the reactive particle.

2. Diffusion of lime to the boundary of the reactive particle.

3. Diffusion of alkali through the reacted rim of the opal particle, partly by diffusion through the interstitial liquid phase and partly by surface diffusion.

4. Diffusion of lime through the reacted rim of the opal particle, mainly by surface diffusion.

5. Diffusion of dissolved silica through the reacted rim to a place in the concrete where calcium silicate can be precipitated.

Hirche and Wolff [63] suggested a diffusion model for ion migration in alkali-silica reaction. According to them,

diffusion of alkali and calcium ions into siliceous
particles takes place in existing voids, at surface,
interface and in the lattice itself. In the case of medium
to large size pores, solvated ions, including their
hydration envelopes, enter the pores due to the difference
in chemical potential. In small pores or along lattice
defects, ions migrate with at least a partial loss of their
hydration envelopes. Since diffusion into the voids is
faster than diffusion into the crystal lattice, diffusion
and reaction in reactive aggregate depend on the structure
of the aggregate. In addition to diffusion, alkali and
calcium ions in the pores or disturbed lattice might go into
exchange with Si-OH groups in the lattice. Alkali ions are
exchanged reversibly to form an unstable phase, while
calcium ions irreversibly form, with the silica lattice,
stable calcium hydrosilicate or calcium silicate.

Compositional variation of the reaction product around
the reactive particles may be explained by the mechanism of
diffusion. Once the reaction product is formed around the
particle future reaction will depend on diffusion of alkali
and calcium ions from the outer boundary to the inner part.
Since the solubility of calcium hydroxide is depressed by
the presence of alkali hydroxides, diffusion of calcium ions
is delayed until the formation of alkali-silica solution
which locally reduces the pH [31]. Furthermore, the

diffusion rate of alkali ions is faster than calcium ions because calcium ion has a large ionic radius and stronger electrostatic attraction to the lattice atoms for its doubly charged ion [63]. Therefore, the alkali content at the inner interface is greater than the calcium content.

However, French [45] argued that the diffusion model can not alone account for all the features observed in the reaction zone. He argued that diffusion is not controlled by concentration gradients because the alkali concentration in the reaction product is higher than that of the cement paste, and the alkali content of the paste is not greatly reduced near the reaction zones. Moreover, he pointed out that diffusion generated by chemical potential gradient can not produce chemical discontinuities and the concentration profiles can not be discontinuous. He, then, proposed a reaction mechanism which is governed mainly by migration of solvent towards a hygroscopic medium. The concentration profile is shown in Figure 3. It is assumed that the stable cement hydrates constitute the inert phase and the pore solution is the mobile phase. Silicon atoms in reactive aggregate have relatively high solubility in alkaline solution. Slow diffusion of dissolved silicon out of the reactive particles results in an attraction of the fluid carrying the alkali ions. Alkali ions thus migrate slowly into the aggregate. Sharply defined zones of high alkali

concentration near the aggregate fragments are then developed. The formation of alkali-silica gel continues to promote the influx of pore solution until the gel becomes mobile and leaves the site of generation. The solubility of reactive aggregate in alkaline solution determines the reactivity.

Reaction products

The reaction product resulting from an alkali-aggregate reaction is considered to be an amorphous gel with no fixed chemical composition, varying from place to place, even within a particular concrete [31]. The reaction product is essentially composed of silica, alkalis, calcium, and various amount of water. Its composition depends on rate of gel formation, rate of ion diffusion, curing time, concrete mix design, concentrations of available reacting ions, exposure conditions, and many other variables [10, 31, 116]. Gel formed in the early stages contains a high silica concentration and more total alkalis than calcium, whereas a gel found in old concrete tends to be calcium-rich and to have a moderate to low alkali content [16, 43, 46]. Gel around the reacting particle is supposed to have a high SiO_2 content and a low level of CaO content; the CaO content is increased with distance from the reacting particle [81, 135]. By quantitative analysis, Knudsen and Thaulow [81] found a linear relationship between the weight percentages
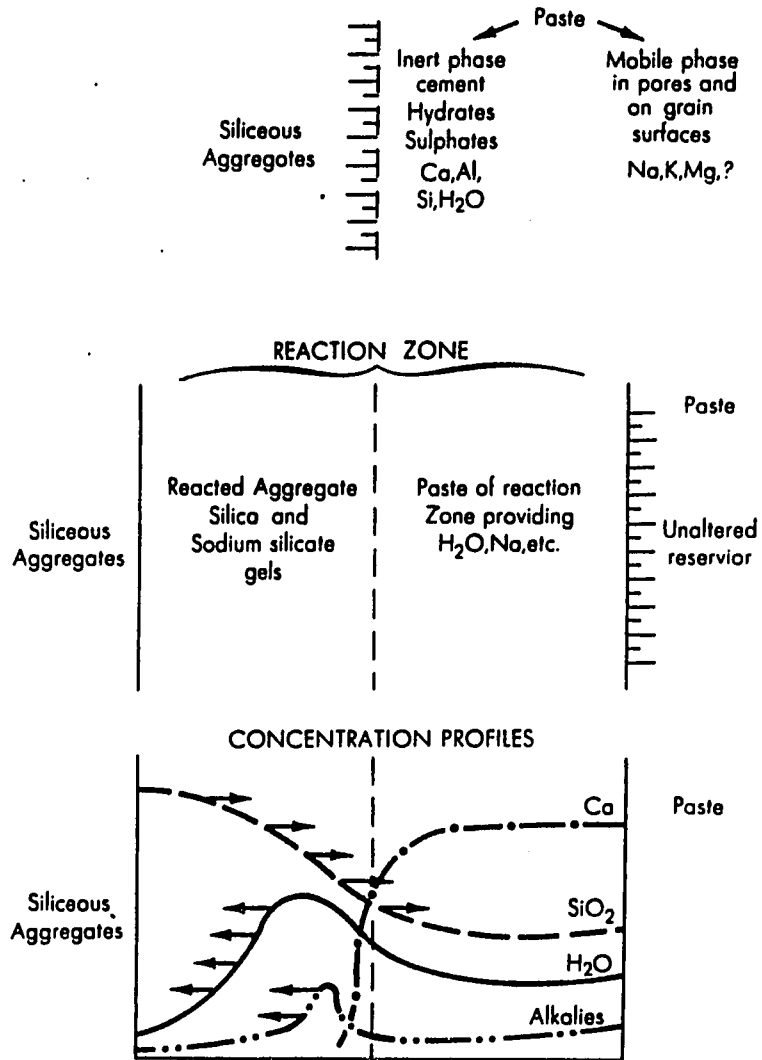
FIGURE 3. Schematic representation of alkali-silicate reaction in terms of solvent migration [45]

of CaO and SiO$_2$ in gel composition. Diamond [28] divided the gel into the following three categories, based on its composition: (1) true alkali-silica gel, (2) lime-alkali-silica gel of low lime content, and (3) lime-alkali-silica gel of high lime content.

The initially formed clear alkali-silica gel may react with free lime released from cement hydration to form a white, opaque and relatively insoluble lime-alkali-silica gel [46, 75, 116, 143, 147]. Powers and Steinour [117] gave a hypothesis to explain safe and unsafe reaction products in concrete expansion, the safety of the products depending on the calcium and alkali contents of the gel. The unsafe gel, having high-alkali and low-calcium contents, can imbibe water to produce expansive pressure in concrete. The safe gel, having a high calcium content, is relatively insoluble and produces less expansion. However, Struble and Diamond [132] found a variable swelling ability in gels with different calcium contents.

Swelling caused by the alkali-aggregate reaction depends not only on the quantity but also on the rigidity (viscosity) of the reaction product [144]. The reaction product can exist either in the form of a gel or in a sol state depending on the water content. When water and alkali concentrations are not too high, a highly viscous gel is formed in the early stages and is followed by an imbibition

of water to convert the gel gradually to a sol which can penetrate into the cement matrix or voids to reduce expansion [26, 46, 82, 94]. According to Vivian [143] and Krogh [82], the volume of the reaction product depends almost entirely on its water content, and the rate of water absorption is inversely affected by the initial water content of the gel. As the reaction product absorbs water, it expands first as a solid gel until its water content is about 40%, and it is to be subjected to a plastic flow when its water content is between 40 to 70%.

Mechanism of concrete expansion

The expansion of concrete is due to the development of alkali-silica gel. The gel imbibes water and increases its volume to produce expansive pressure greater than the tensile strength of concrete and cracks the concrete.

Hansen [59] proposed the hypothesis that expansion is associated with osmotic pressure generated by reaction products which are confined within a semi-permeable membrane of cement paste. This semi-permeable membrane permits water and the ions and molecules of the alkali hydroxide to diffuse through it, but it does not permit the diffusion of silicate ions. Since reaction products imbibe water that increases their volume, and the silicate is not permitted to diffuse out through the cement paste, a hydrostatic pressure is developed to produce cracking. A number of researchers

[26, 94, 95, 116, 136] agree with Hansen's hypothesis that osmotic pressure could be generated by such means. However, Vivian [139] and Jones and Vivian [76] pointed out that membranes were not formed across cracks and high swelling pressures were not developed inside the membrane. The expansion was mainly caused by the formation and subsequent widening of cracks due to mechanical pressure exerted by the reaction products.

Sources of Alkalis and Their Limitations in Concrete

Cement

The main source of alkalis, sodium and potassium, which induce alkali-aggregate reaction in concrete is their generation during cement hydration. Diamond [27], McCoy and Eshenour [96], Jawed and Skalny [70], and Vivian [148] have reviewed and discussed the origin and forms of alkalis in cement and their effects on clinker formation. The alkalis in cement are mainly originated from the siliceous and argillaceous raw materials (such as: clay, shale, chalk, and limestone) and the coal ash if coal is used as the primary fuel. Alkali compounds in clinker are affected by the presence of sulfate, and they can be divided into three groups depending upon the amount of sulfate: (1) alkali sulfate, (2) alkali aluminates and aluminoferrites, and (3) alkali silicates. In the presence of excess sulphur, most

alkalis are present as sulfates, such as potassium sulfate (K_2SO_4), sodium potassium sulfate ($Na_2SO_4 \cdot 3K_2SO_4$) or calcium potassium sulfate ($CaSO_4 \cdot K_2SO_4$) in which potassium generally predominates over sodium in the sulfate form. When the amount of sulphur is insufficient to bind all alkalis in the form of sulfates, the alkalis tend to combine with dicalcium silicate (C_2S) to form $K_2O \cdot 23CaO \cdot 12SiO_2$ ($KC_{23}S_{12}$) and with tricalcium aluminate (C_3A) to form $Na_2O \cdot 8CaO \cdot 3Al_2O_3$ (NC_8A_3) together with sodium sulfate-potassium sulfate solid solution. According to Jawed et al. [71], almost all Na_2O present in the Na_2O-C_3A solid solution tends to be released into the pore solution at the same rate as the dissociation of the solid solution.

The ASTM Standard Methods for Chemical Analysis of Hydraulic Cement (C 114) provides test methods to determine the water soluble and acid soluble alkali contents in cement. The ASTM Specification for Portland Cement (C 150) suggests a maximum of 0.6 percent of total alkali content, expressed as equivalent Na_2O (% Na_2O + 0.658 X % K_2O), when the cement is to be used in combination with reactive aggregates. Since the cement content in concrete directly controls the availability of alkalis in the alkali-aggregate reaction, however, the specification does not take into account the mix proportion of cement in a particular concrete. Thus, some researchers convert alkali content

into the amount of alkalis contained in a unit volume of concrete, Kg/M^3. According to Hobbs [66], cracking of mortar occurs when the water soluble alkali content is greater than 2.5 Kg/M^3 or the acid soluble alkali content is greater than 3.25 Kg/M^3. For Malmesbury aggregate in South Africa, Oberholster [109] found that an alkali content above 3.8 Kg/M^3 was deleterious, between 3.8 and 1.8 Kg/M^3 was potentially deleterious, and below 1.8 Kg/M^3 was safe.

Mineral admixture

Addition of mineral admixtures to concrete is frequently used to mitigate the deleterious expansion due to the alkali-aggregate reaction. However, a certain amount of alkali may be released from the admixture itself; this enhances the reaction. ASTM C 311 provides a test method to determine the amount of alkalis that will be available from the admixture. It consists of reacting 5 grams of fly ash, 2 grams of calcium hydroxide and 10 ml water for 28 days at 38°C, extracting the available alkalis with water and determining their concentration with flame photometry. The use of fly ash or other pozzolan is governed by ASTM C 618 which specifies that the maximum allowable available alkali content, instead of total alkali content, is 1.5% equivalent Na_2O.

When granulated blastfurnace slag is used to counteract alkali-aggregate reaction, the expansion depends on the slag

content and the total alkali content. A limit of 0.9% of total alkali content is allowed when at least 50% of slag is used in concrete, and 2% of total alkali content is the upper limit for slag cement with at least 65% slag.

Other sources

It should be noted that alkalis from other sources may have the same effect on the alkali-aggregate reaction. Possible sources of alkalis are alkali containing aggregate [60, 130], silicate glass [10, 41], mixing water, sea water or de-icing salt [42, 48, 82, 114, 125]. Unfortunately, no specification is available which sets limits on alkalis from those minor sources.

Factors Which Influence Alkali-Aggregate Reaction

Effects of reactive aggregates

Size   For aggregates involved in the alkali-silica reaction, the amount of expansion tends to increase as the reactive grain size decreases when a certain amount of reactive aggregate is used. This is due to the smaller particles having greater surface area with which to react with the alkalis [11, 34, 66, 78, 146]. When the size of reactive particles is sufficiently small (less than No. 300 sieve), expansion is prevented because the reactive particles act as a pozzolan [7, 117, 146]. However, Diamond and Thaulow [34] found that those pozzolan size particles

may produce serious expansion if they are present in appropriate proportions. Comparing rates of expansion, samples containing larger reactive particles expand slower and have greater local expansive pressure than samples containing smaller reactive particles [34, 78, 86]. Lenzner and Ludwig [87] observed a maximum expansion for opaline sandstone when the grain size was in the range of 0.5-1.0 mm as compared with other grain sizes. They explained this by the existence of an optimum available alkali and calcium ion concentrations for reacting particles to form the most expansive reaction product, and the existence of a maximum overlaping expansive pressure when the grain size was in this range.

For slow expanding aggregates involved in the alkali-silicate reaction, the amount of expansion measured in concrete prism tests increased with increasing reactive aggregate grain size [39, 52]. The reason is not clear, but it might be attributed to less volume increase and greater restrain from cement paste for smaller grain size of reactive aggregate.

Amount   For a given mix, Stanton [128] found that expansion increases with increasing reactive aggregate content until a maximum expansion has been reached. Expansion then decreases with further increase in the reactive aggregate content. The reactive aggregate content

producing the maximum expansion, the so called pessimum content,[1] is greatly influenced by the cement alkali content as well as by the grain size and the type of aggregates. The pessimum content tends to shift to a higher proportion when the cement alkali content or the grain size is increased [112, 125]. The pessimum content varies widely for different types of reactive aggregate [50, 140]. A small pessimum content may be obtained when the aggregate is highly reactive [90, 125], or when the aggregate shows considerable reduction in alkalinity in the ASTM chemical method (C 289) [101]. Mathematical models to predict mortar bar expansion have been studied and discussed by Hobbs [64, 65] and French [46].

Mielenz et al. [101] interpreted the pessimum phenomenon as the result of two opposing characteristics of the alkali-aggregate reaction. The first of these is the tendency for increased expansion of mortar as more reactive particles are made available for attack. The opposing tendency is that the alkali available for reaction at each site decreases with increasing amounts of reactive particles.

---

[1] A term which describes the content of a specified component, such as: aggregate, alkalis or mineral admixtures, in concrete or mortar to produce maximum expansion.

Porosity   Since the reaction products with low

viscosity can penetrate into the aggregate pores to reduce

the expansive pressure, a highly porous aggregate produces

less expansion than a dense aggregate [100, 125]. Ludwig

[90] found that expansion of mortar bars is prevented when

the porosity of opaline sandstone is greater than 40% by

volume, and expansion increases with decreasing aggregate

porosity

Effects of alkalis

Content   Vivian [142] reported that there is a

pessimum alkali content for expansion caused by alkali-

aggregate reaction. For a given amount of opal in the

system, expansion increases with increasing alkali content

up to a certain level. Beyond this level, a large addition

of NaOH to the system can reduce expansion because the

reaction products with a high Na_2O/SiO_2 mole ratio transform

to fluid rapidly after imbibition of water. Thus, expansive

pressure is reduced by penetration of fluid reaction

products into the cement matrix. Baker and Poole [3]

suggested that the formation of calcium silicate hydrates,

which control the migration of alkali ions to a reactive

particle, cease to develop completely when the alkali

content is beyond the pessimum content. Expansion is

reduced by allowing excess alkali ions to reach the reaction

site and to change the ideal composition of alkali-silica

gel required to produce maximum swelling. According to
Lenzner [86], samples with higher alkali content show
earlier rehealing than samples with lower alkali content by
the measurement of resonance frequency. In Verbeck and
Gramlich's osmotic studies [136], solutions with high alkali
concentrations showed less mobility through the cement paste
than do solutions with lower concentrations.

Type   Davis [21] found that potassium hydroxide
produces more rapid reaction than sodium hydroxide at early
stages, but that sodium hydroxide shows more total expansion
than potassium hydroxide at later stages. In a rapid
chemical test studied by Mielenz et al. [101], the use of
KOH solution showed less reduction in alkalinity and less
solubility of silica than the use of NaOH solution. Osmotic
studies show that potassium hydroxide has the highest flow
rate, followed by sodium hydroxide and lithium hydroxide.
Krogh [82] found that smaller expansion is obtained when K_2O
is the predominating alkali oxide in the system than when
Na_2O predominates. Hansen [62] pointed out that the
reaction product $K_2Si(OH)_6$ requires much less water for
dissolution than $Na_2Si(OH)_6$. Consequently, sodium ion is
more destructive to aggregate than potassium ion at an
equivalent concentration, and more potassium content in
cement can be tolerated than equivalent sodium content.
Note, that the alkali reactivity of cement-aggregate

combinations depends mainly on the total alkali content in cement, usually expressed as equivalent Na_2O, rather than individual alkali content.

Addition of lithium salts to concrete appears to reduce the expansion caused by alkali-aggregate reaction [83, 95]. Hansen [61] reported that the soluble silicates produced by Na_2O and K_2O attack may be converted to insoluble silicates by the presence of Li_2O; insoluble silicates produces less expansion than soluble silicates.

Effects of mix proportions

Mortar expansion is greatly dependent on the porosity of the mortar which is in turn controlled by the proportions of cement, aggregate, and water. A minimum porosity of mortar between 7 to 15% by total volume could inhibit expansion because the reaction products are allowed to penetrate into the voids and to reduce expansive pressures [13, 85, 86, 126, 138]. Introduction of an air-entrainment agent into concrete may also reduce expansion caused by the alkali-aggregate reaction, but the effectiveness of protecting concrete from freeze-thaw damage may be reduced [73].

Vivian [138] found that expansion increases with increasing W/C ratio up to a certain level. Beyond that level, expansion decreases with increasing W/C ratio. Since the ion concentration is inversely proportional to the W/C

ratio, the reaction will start more rapidly when the W/C
ratio is low [87].

The alkalis existing in concrete are mainly released
from the cement minerals so that increasing the proportion
of cement also increases the quantity of alkalis which
accelerates expansion [11, 15]. Hence, to avoid deleterious
alkali-aggregate reactions in the particle structure, not
only the limitation of alkali content in cement should be
considered but also the respective cement content of the
concrete [44, 125].

Effects of humidity

Water behaves as the solvent and the transport medium
for reacting ions taking part in the reaction [103]. The
swelling properties and the volume of reaction products are
greatly dependent on the water content. Thus, mortar
expansion depends very largely on the amount of water that
is available [82, 141].

Nilsson [103] reported that a very high swelling
pressure could be obtained from subsequent humidification of
a relatively dry gel with high viscosity when a certain
humidity exists around the reactive aggregate. Lenzner and
Ludwig [87] have studied the moisture dependence of
expansion due to the alkali-silica reaction. Their results
indicated that the minimum relative humidity required for
expansion is about 85%, and a poorer water supply does not

diminish the expansion, but only delays the damages.

If the reaction does not take place completely, one of
the most detrimental environments in the field is one of
repeated drying and wetting cycles [12, 31, 87, 107]
because: (1) high local alkali concent.ation may be
developed from moisture migration through the concrete and
evaporation near the surface, (2) the cement structure is
more stiff at the time of swelling and limited swelling
pressure can be released by plastic deformation of concrete,
and (3) the rate of swelling is higher since a large amount
of reaction products are already formed at the time of
taking water. When the concrete is continuously immersed in
water, the amount of expansion can be minimized by the
reduction of the alkali content due to diffusion and
leaching, and by the rapid transformation of gel to sol in
the presence of excess water [147].

Effects of temperature

The rate and amount of expansion caused by alkali-
aggregate reaction are greatly dependent on the storage
temperature. Increase of temperature generally accelerates
the reaction, but the amount of expansion will be decreased
as temperature is raised beyond a certain level [11, 88,
129]. It has also been found that the amount of long term
expansion for samples cured at an elevated temperature
(38°C-40°C) was less than the samples cured at room

temperature [35, 47, 86, 87, 90, 105, 145]. The temperature to produce the maximum expansion varies with type of aggregate [39, 57, 78, 129]. ASTM currently specifies a curing temperature of 38°C in many standard test methods.

Vivian [143, 145] reported that the temperature affects the rigidity of the reaction product and the rate of water absorption by the product. During the initial periods, the reaction product has a low water content and is relatively rigid. Elevated temperatures accelerate the rate of water absorption resulting in higher rate of expansion. However, the reaction product with higher water content at high temperatures is more mobile than that at lower temperatures. When the reaction product becomes more mobile it flows through the cracks produced during the initial expansion. Therefore, the total amount of expansion at higher temperatures is smaller than that at low temperatures because of the smaller proportion of reaction product has sufficient rigidity to exert swelling pressures.

In consequence, one should be careful to interpret the accelerated test results obtained from high temperature condition.

Effects of other factors

Loading   Application of restraints on concrete such
as reinforcements tends to change the pattern, initiation,
and propagation of cracks [12, 97]. When the applied load
is sufficiently large, the major cracks tend to be aligned
with the direction of load action or the direction of the
major principal stress in concrete. Since the amount of
absorbed water and the volume change of reactive particles
can be reduced by increasing the applied forces, the amount
of expansion and the width and number of cracks tend to be
reduced by increasing the applied forces.

Dimension   Alkali-aggregate reaction in massive
concrete can be accelerated and promoted by slow dissipation
of hydration heat, longer time required for drying and the
penetration of moisture through thermal cracks [44]. Thus,
Bakker [5] recommended to use larger specimens with cross
section greater than the distance between cracks in
expansion tests to decrease the risk of missing reactive
aggregates.

Cement fineness   The use of a finely ground cement
induces larger expansion than a coarsely ground cement
because the release of alkalis from a finer cement is faster
than from a coarser cement [11].

Chemical additives   Mehta [98] studied the effects
of different chemical additives on alkali-aggregate

reaction. He found that sodium salts produce greater expansion than potassium salts, and expansion decreases with type of anion combined with alkalis in the order of sulfate, chloride, carbonate, and nitrate.

Lenzner [85] studied the effects of two alkali-bearing plasticisers. He found that the rate of expansion is significantly increased by the addition of plasticisers, but the deterioration is less than the reference mortar.

pH   According to Figg [41], the rate of alkali attack in concrete increases very rapidly when pH value in pore solution is above about 10, and the effect of pH is very small when its value is below 9.

Test Methods of Avoiding the Use of Alkali-Reactive Aggregates

The use of non-reactive aggregate to protect concrete from alkali-aggregate reaction is common in practice. Thus, to avoid the use of reactive aggregate in concrete, it is necessary to identify which aggregate is reactive, potentially reactive, or innocuous. A flow chart, shown in Figure 4, provides procedures to select test methods for identifying the alkali-reactivity of aggregates usually used by engineers.

```
                              ┌─────────────────┐
                              │   aggregates    │
                              └─────────────────┘
                                       │
                                       ▼
high content of                    ╱◇╲
reactive components      ◄────────╱  petrographic  ╲────────►  non-reactive
                                  ╲  examinations  ╱
                                   ╲◇╱
                                       │
                                  doubtable
                                  aggregates
                                       │
                                       ▼
potentially                        ╱◇╲
deleterious              ◄────────╱   chemical   ╲────────►  non-reactive
                                  ╲    method    ╱
                                   ╲◇╱
                                       │
                                       ▼
potentially                 ╱─────────────────────╲
deleterious      ◄─────────╱  mortar bar method,   ╲──────►  non-reactive
                           ╲  concrete prism method, or ╱
                            ╲  reliable accelerated test ╱
                             ╲─────────────────────────╱

      ┌─────────────────┐              ┌─────────────────┐
      │   preventive    │              │  suitable for   │
      │   measures      │              │  use as concrete│
      │                 │              │  aggregate      │
      └─────────────────┘              └─────────────────┘
```
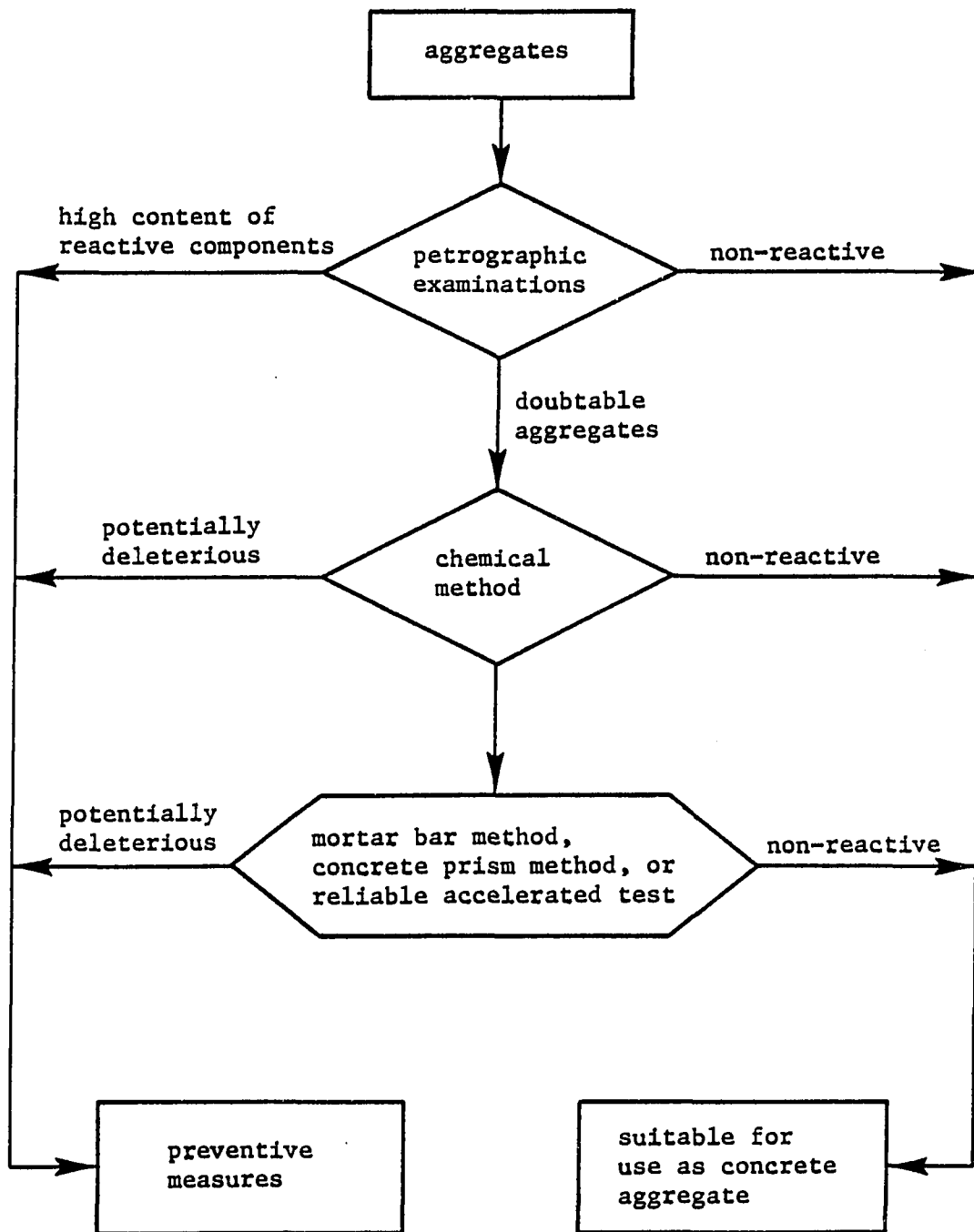
FIGURE 4. Flow chart of selection test methods for avoiding
           the use of alkali-reactive aggregates

Petrographic examination

According to Sims [120], the purpose of petrographic examination is to "identify any constituents that are potentially susceptible to alkali-reactivity, to derive a preliminary view of the likelihood of deleterious reaction by informed consideration of the relative proportions, and to indicate the most appropriate form of subsequent testing when this is deemed to be necessary." The ASTM Recommended Practice for Petrographic Examination of Aggregate for Concrete (C 295) [2] provides guidance of sampling techniques and examinations for gravels and sands, drilled cores, crushed stones, and manufactured sands. Petrographic examination is recommended to be performed by well educated and experienced petrographer with help of optical microscopy, X-ray diffraction analysis, differential thermal analysis, infrared spectroscopy, or scanning electron microscopy.

Chemical method

ASTM recommends a standard test for Potential Reactivity of Aggregates (Chemical Method) (C 289) [2] which was originally studied by Mielenz et al. [101] as a rapid means of differentiating between potentially reactive and non-reactive silica-bearing aggregates. The chemical method consists of measuring the amount of silica dissolved (S_c) in 25ml 1N sodium hydroxide solution from 25g aggregate sample

(crushed to No. 50 to No. 100 sieve size range) reacted at 80°C for 24 hours, and the concomitant reduction in alkalinity (R_c) of the solution. The reactivity of aggregates is then determined by a decision chart listed in ASTM C 289 and shown in Figure 5. Roughly speaking, the potentially deleterious aggregates are those with which a large reduction in alkalinity is accompanied by a correspondingly large production of soluble silica, whereas the deleterious aggregates show a modest lowering of the alkalinity accompanying a considerable production of soluble silica [26]. ASTM C 33 gives the criteria for chemical test as:

1. If R_c exceeds 70, the aggregate is considered potentially reactive if S_c is greater than R_c

2. If R_c is less than 70, the aggregate is considered potentially reactive if S_c is greater than $35 + (R_c/2)$.

The chemical test is a good method to screen the reactivity of aggregate because the results can be obtained within 3 working days, small quantities of sample are required for the test, and it gives apparently clear results in majority of cases [120]. However, there are some factors which may influence the test and give misleading results. Since the aggregates are neither pure nor monomineralic materials, the mineral components other than reactive silica, such as calcium, magnesium or ferrous carbonates or sulphates, in the aggregates may also react with NaOH resulting in larger reduction in
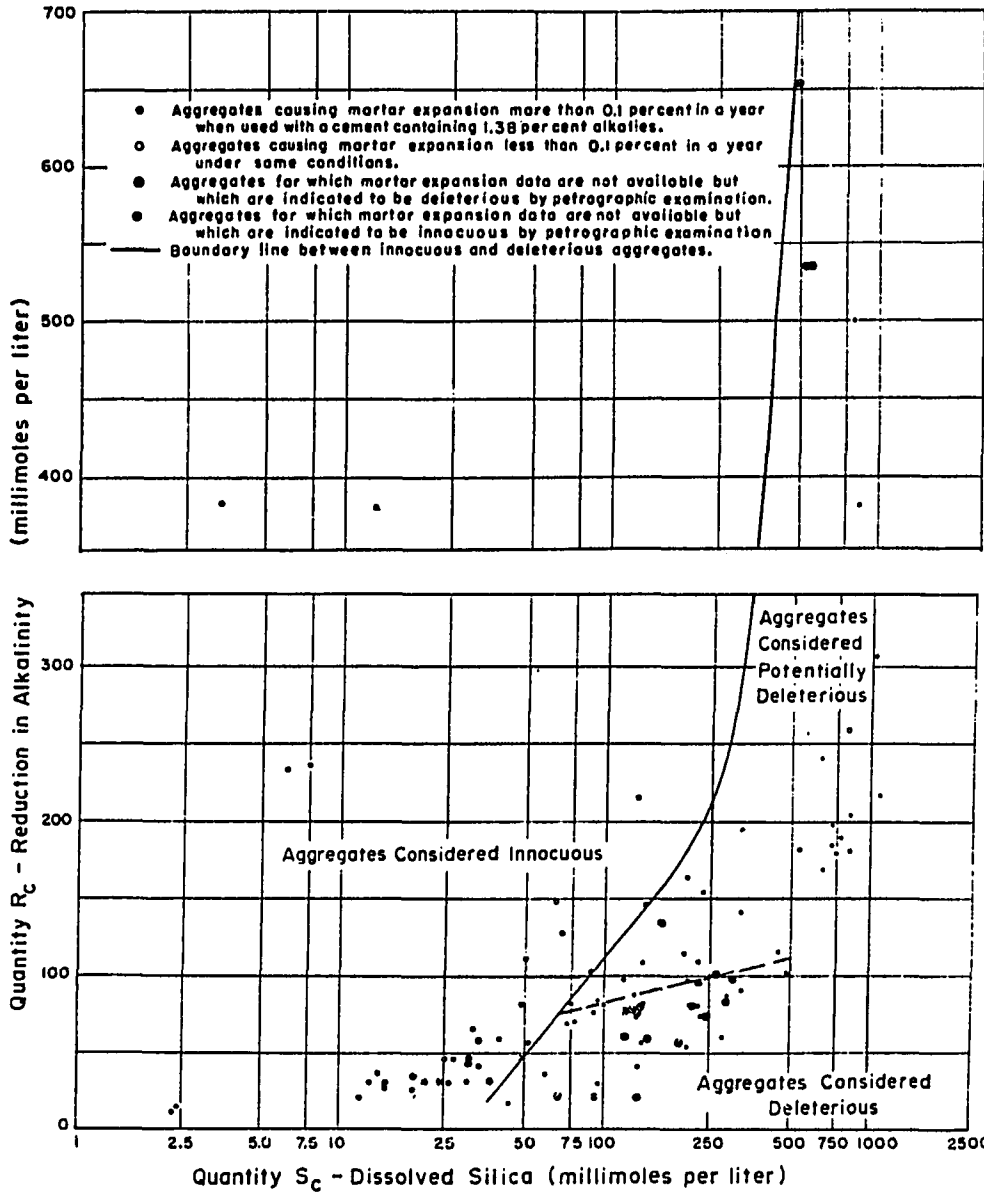
FIGURE 5. Illustration of division between innocuous and deleterious aggregates on the basis of ASTM C 289 chemical method [2]

alkalinity of the solution [26, 54, 152]. The aggregates are likely to contain variable amounts of exchangeable cations adsorbed on clays which may remove alkalis from the NaOH solution. Poor reproducibility of the test may originate from poorly sized samples because smaller particles may considerably increase the concentration of dissolved silica [54, 80]. Because the phenolphthalein indicator does not give a sharp end point, determination of the value of reduction in alkalinity is somewhat dependent on the judgement of the operator. Furthermore, the value of reduction in alkalinity obtained includes reduction in both OH^- and Na^+ concentrations in the solution. It is suggested to measure OH^- by a pH meter and Na^+ by a spectroscopic method [23]. Consequently, Vivian [147, 152] suggested that the amount of dissolved silica should be considered as the pre-dominant factor and the alkalinity reduction is less significant to determine the potential reactivity of aggregates.

The chemical method was originally developed for determining the alkali reactivity of certain siliceous rocks, minerals and glasses with which alkali-silica reaction takes place. This method is not adequate for the evaluation of aggregate which induce alkali-silicate reaction and alkali-carbonate reaction as categorized by Gillott [48]. Brandt et al. [14], Duncan et al. [39], Grattan-Bellew [54], and Oberholster [108, 109] have reported their studies and their

recommendations concerning the chemical test method for aggregate producing alkali-silicate reaction.

Mortar bar method

ASTM test for Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar-Bar Method) (C 227) [2] is commonly used for evaluating the potential alkali reactivity of aggregate. 1" X 1" X 11 1/4" mortar bars are made using crushed aggregate with specified gradation and a high-alkali cement (or job cement) with the aggregate/cement ratio of 2.25. The amount of mixing water is controlled to produce a flow number between 105 and 120. After one day moist curing, mortar bars are stored in sealed containers designated to maintain 100% relative humidity at 38°C for desired periods. It is recommended that cement-aggregate combinations, which expand more than 0.10% in 6 months, or 0.05% in 3 months, are considered capable of deleterious reactivity.

Although the mortar bar method requires a relatively long time to obtain reliable results, the test has such advantages as [149]:

1. The test is non-destructive.
2. The specimen can be measured and examined visibly at desired time intervals.
3. The progressive changes can be observed during the entire test period.
4. The usual reaction signs such as the appearance of

wet reaction spots, gel exudations, surface pop-
outs, and expansion cracks can be observed
simultaneously with the test.

Even though ASTM C 33 recommends to use a cement with
total alkali content preferably above 0.8% for the test, the
test still has some uncertainties [14, 108, 120] which are:

1. The total alkali content is not necessarily a
   measure of the active alkalis which can be available
   in the reaction.

2. It is not specified that criteria still apply or
   should be adjusted when a cement with higher or
   lower alkali content is used.

3. Other components contained in cement instead of
   alkalis, such as calcium hydroxide and tricalcium
   silicate, may also have effects on alkali
   reactivity.

4. The reactivity of cement is not specified, and the
   cement itself can expand to a certain extent.

Because of the uncertainties concerning the cement itself,
Brotschi and Mehta [15] proposed two test methods for
determining potential alkali-silica reactivity in cements.
Stark [130] suggested to use cement with a range of high and
low alkali content, and to extend the test period to twelve
months.

Criteria listed in ASTM C227 are satisfactory for aggregates showing alkali-silica reaction, but they seem to underestimate for some slow expanding aggregates which exhibit alkali-silicate reaction. Some slow expanding aggregates even mixed with high-alkali cement may show expansions well below the value considered to be deleterious, but they expand continuously leading to damages [14, 39, 52, 55, 108, 111, 120, 130]. It is recommended that the test should be continued until either the rate of length change becomes negligible or the expansion possess a predetermined level [120]. Some other criteria proposed for identifying reactive aggregates are summarized in Table 1.

Concrete prism method

Evaluation of alkali-reactivity for slow expanding aggregates, which fails to be detected by mortar method, can be successfully evaluated by concrete prism method [14, 39, 52, 55, 80, 111]. The concrete prism method is similar to the mortar bar method except that the samples size is larger, and the aggregate gradation is different.

The materials used in concrete prism method can be mixed at the same proportions and aggregate gradation as the actual concrete in construction to eliminate the effect of aggregate size on expansion. Concrete prism method may be reliable to evaluate alkali-reactivity for all types of aggregates including siliceous and carbonate aggregates [52, 53, 54, 55].

TABLE 1. Criteria for mortar bar method under ASTM C 227
         specification

Source	Type of aggregates	Criteria for reactive aggregates (% expansion[a])
ASTM C 227 [2]	siliceous aggregates	1. > 0.05% at 3 months 2. > 0.10% at 6 months

Blanks and Meissner [11]	siliceous aggregates	1. non-reactive:
		   < 0.02% at 6 months
		2. potential reactive:
		   0.04% at 6 months
		3. reactive:
		   > 0.10% at any ages

Bredsdorff et al. reviewed by Kennerley et al. [79]	New Zealand aggregates	> 0.10% at 24 months
Canadian Standards reviewed by Grattan-Bellew [54]	siliceous aggregates	> 0.04% at any ages
Corps of Engineers reviewed by Grattan-Bellew [54]	siliceous aggregates	1. > 0.10% at any ages 2. > 0.05% at 6 months
Duncan et al. [39]	Nova Scotia aggregates	> 0.05% at 72 weeks
Grattan-Bellew [53]	siliceous aggregates	expansion rate > 6.4×10^{-3} %/day$^{-\frac{1}{2}}$
Majid and Grattan-Bellew [91]	Iraq aggregates	regression line slope > 18×10^{-5} %/day
Oberholster et al. [111]	Malmesbury aggregates	1. > 0.04% at 72 weeks 2. > 0.05% at 144 weeks
Vivian [147, 152]	siliceous aggregates	> 0.05% within 12 months

[a] Unless specified otherwise.

However, large storage space required and long time for curing are major disadvantages of the test.

As compared with mortar bar method, concrete prism method still has the same problems of cement uncertainties. Even though no world wide accepted criteria are available, several criteria have been proposed for concrete prism method to evaluate the alkali-reactivity of aggregates which are shown in Table 2.

Accelerated test methods

Since both mortar bar and concrete prism methods require long periods of time to get useful results, attempts have been made to decrease the time required for the tests by arbitrarily controlling the test conditions. In general, the test can be accelerated by increasing alkali content internally or externally, controlling W/C ratio, elevating storage temperatures, or limiting the amount of reactive component in aggregate and the sizes of reactive particles. However, it should be noted that accelerated test methods do not always modify the test consistently, and one should be careful to interpret the results.

Alkali solution bath methods   Chatterji [18] suggested a NaCl bath method to evaluate alkali-reactivity of aggregates, and Jensen et al. [72] confirmed that this method performed satisfactorily for Danish sands. They found that the expansion rates of 40 x 40 x 160 mm mortar bars were significantly

TABLE 2.   Criteria for concrete prism method cured at 100%
           relative humidity

Source	Brief description	Criteria for reactive aggregates (% expansion[a])
Brandt et al. [14]	size: 3"x3"x12" A/S/C/W[b]= 3.4:1.9:1.0:0.5 temp.: 38°C aggregate: Tygerberg Formation aggregates	> 0.05% at any ages
Bureau of Reclamation reviewed by Oberholster [111]	siliceous aggregates cured in sealed container at 55°C	> 0.07% within 120 days (17 weeks)
Canadian Standards reviewed by Grattan-Bellew [54]	slow expanding aggregates	> 0.03% at any ages
Duncan et al. [39]	size: 3"x3"x11" strength: 3,500 psi slump: 2-3 in. max. agg.: 3/4 in. W/C: 0.6 temp.: 38°C alkali content: > 0.9% aggregate: slow expanding aggregates	> 0.05% at 120 weeks
Grattan-Bellew [52, 53]	size: 3"x3"x10" max. agg.: 19 mm. W/C: 0.40 to 0.45 temp.: 38°C aggregate: slow expanding aggregates	regression line slope > 20×10^{-5} %/day or > 3.55×10^{-3} %/day$^{-\frac{1}{2}}$

[a] Unless specified otherwise.

[b] A/S/C/W = aggregate/sand/cement/water.

increased when mortar bars were immersed in a saturated NaCl
solution at 50°C after 28 days of water curing. However, no
criteria are available for this method.

Another alkali solution bath method was proposed by Ardt
and Visser and reviewed by Oberholster [109]. Mortar bars,
prepared in accordance with ASTM C 227, were immersed in 1 N
NaOH solution at 80°C for 14 days. They suggested that
expansion of mortar bars greater than 0.08% but less than 0.2%
at 14 days indicated a slowly expansive siliceous aggregate,
whereas expansion greater than 0.2% indicated a readily
expansive aggregate.

Autoclave method   Tang et al. [134] suggested an
autoclave method to accelerate the test for evaluating alkali-
reactivity for aggregates. 1 X 1 X 4 cm. mortar bars were
cured in 100°C steam for four hours, and then autoclaved in 10%
KOH solution for six hours. Expansions were measured after
each phase of curing cycle. No criteria were given for this
method. Although results could be obtained by this method
within 2 days, caution should be taken because of the observed
expansion might be disordered by hydrothermally induced
reactions which would not occur in concrete under normal
conditions [54].

Miscellaneous methods

Gel pat test   Gel pat test, proposed by Jones and
Tarleton [75], consists of observing the growth of white gel on
the ground surface of a neat cement paste containing embeded
aggregate particles. The pat is immersed in mixed alkali
solution containing 0.5N NaOH and 0.5N KOH and saturated lime
at 70°F. The growth of white gel could be found on the embeded
aggregate particles within a few days for highly reactive
aggregates such as opal, but a long period of curing is still
needed for slow reactive aggregates such as flint or some
limestones.

As reviewed by Grattan-Bellew [54] and Sims [120], the gel
pat test is an useful rapid test for primary identification of
alkali-reactive aggregates, especially for opal bearing
aggregates. However, it does not necessarily mean that the
aggregate will be deleteriously reactive in concrete when white
gel grows on the aggregate particles. Therefore additional
mortar bar tests are needed to confirm the reactivity of the
aggregate in concrete.

Osmotic cell test   Stark [131] suggested an osmotic
cell test which was originally studied by Verbeck and Gramlich
[136], to evaluate alkali-aggregate reactivity. The cell
consists of a reservoir chamber and a reaction chamber
separated by a cement paste membrane. Both chambers are filled
with 1N NaOH solution to the same height in the two capillary

tubes attached to the top of both chambers, except that the
reaction chamber also contains a 12 grams of test sample sized
in the range between No.50 and No.100 sieves. The reactivity
of aggregates is obtained by measuring the flow rate, expressed
as height difference between the two capillary tubes, of NaOH
solution from the reservoir chamber through the cement paste
membrane into the reaction chamber. If the flow rate is
greater than 1.5-2.0 mm/day, the aggregate is alkali reactive.
However, a number of uncertainties in the test such as the
permeability and physical and chemical properties of the cement
paste membrane should be specified before this method is widely
accepted.

Determination of undulatory extinction angle

Undulatory extinction (UE) angle measured by light microscopy
is an indication of the degree of deformation in the quartz
crystal lattice which determines the alkali-reactivity of
quartz bearing aggregate. As defined by Dolar-Mantuani [37],
the UE angle is "the angle between the position of clear
evidence of extinction and the position of disappearance of all
shadows read on the graduated microscope stage when rotating it
from the first position to the second position", or, in other
words, is "the angle between the position of first extinction
and the position of almost invisible shadows in quartz read on
the graduated microscope stage". Gogte [51] found that
aggregates containing 40% or more of strained quartz varieties

were highly reactive, those with 30-35% strained quartz varieties were moderately reactive, and aggregates containing unstrained or recrystallized quartz were innocuous. Dolar-Mantuani [37] suggested that the UE angle of quartz bearing aggregates smaller than 15° indicates non-reactive aggregates.

Measurement of resonance frequency   Lenzner and Ludwig [87] and Lenzner [86] measured the resonance frequency (natural frequency) of the mortar bar together with their expansions as the indication of the strength variation and the extend of the damage in the mortar structure. A decreasing resonance frequency indicates a reduction in strength and a tendency of expansion. An increasing resonance frequency indicates the rehealing of the micro-cracks, the strengthening of the mortar structure, and probably the termination of expansion. Therefore, the resonance frequency decreases continuously when the mortar is in expansion process, but the resonance frequency starts to increase when the expansion is stopped.

Use of Pozzolanic Materials to Mitigate the Reaction

When low-alkali cements and non-reactive aggregates are not economically available, addition of a suitable pozzolanic material as a mineral admixture to concrete can successfully eliminate the deleterious effects of alkali-aggregate reaction. According to ASTM C 618, pozzolans are "siliceous or siliceous and aluminous materials which in themselves possess little or

no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties." A suitable pozzolan for preventing alkali-aggregate reaction should be finely ground, have low alkali content, and possess a high degree of reactivity with alkalis [149]. Sufficient amount of a suitable pozzolan, when uniformly distributed throughout mortar or concrete, can react with the active alkalis in pore solution, and the presence of excess unreacted pozzolan tends to safe guard the concrete against delayed reaction and expansion [7]. Fly ash and granulated blastfurnace slag are the pozzolans commonly used in concrete to mitigate the deleterious effects of alkali-aggregate reactions.

Pozzolan particles can react with alkali and hydroxyl ions present in concrete pore solution much faster than larger reactive aggregate particles on account of their larger surface area [31, 87, 99, 147, 150] Thus, the alkali and hydroxyl ion concentrations do not reach a high enough level to attack reactive aggregates. It has been found that alkalis. can be retained in the structure of calcium silicate hydrates (C-S-H) which is the major product from cement hydration and pozzolanic reaction. The amount of alkali retained by these hydrates depends on their lime to silica (C/S) mole ratio. Bhatty and Greening [9] found that low C/S ratio hydrates retain more

alkalis than the high C/S ratio hydrates. Addition of pozzolan with high silica content reduces the C/S ratio of C-S-H, and reduces the amount of alkalis available to react with reactive aggregates [8, 17, 87, 118]. Thus, the use of pozzolan with higher silica and lower calcium contents is more effective to reduce the deleterious effects caused by alkali-aggregate reactions.

Chatterji [19] reported that the presence of free $Ca(OH)_2$ in a damaged concrete is a necessary condition for the breakdown of a concrete caused by deleterious alkali-aggregate reaction. The free $Ca(OH)_2$ content in concrete can be reduced by the addition of pozzolan because the added pozzolan reacts with free $Ca(OH)_2$ to form cementitious compounds. The $Ca(OH)_2$ content in concrete decreases with increasing amount of pozzolan. The greater the amount of free $Ca(OH)_2$ removed by addition of pozzolan, the better the preventive effect of the pozzolan [20, 133]. The alkali-silica gel initially formed around the reactive particles may undergo further reactions with $Ca(OH)_2$ to form lime-alkali-silica gel which is relatively insoluble and produces limiting swelling characteristics [151]. The presence of pozzolan facilitates the mobilization of calcium into reactive particles, and, also, reduces the free $Ca(OH)_2$ content [77].

Tang et al. [133] suggested that the preventive effects are related to the acidity of pozzolan and the basicity of

cement. Among oxides in pozzolan, SiO_2 has the strongest acidity as compare to Al_2O_3 and Fe_2O_3, and CaO is basic. The basicity of cement is the ratio of basic oxides to acidic oxides, $CaO/(SiO_2 + Al_2O_3 + Fe_2O_3)$. Their studies indicated that the stronger is the acidity of the pozzolan, the better is its preventive effect. When the basicity is lower, more alkalis tend to be retained in the hydration products, and less OH^- concentration can be found in the pore solution of cement paste. Hence, when cements have the same alkali contents, the cement with lower basicity will have less vigorous effect on alkali-aggregate reaction.

ASTM C 441 [2] gives a standard procedure for evaluation of the effectiveness of pozzolans in preventing expansion due to alkali-aggregate reaction. It is based on comparison of the 14-day expansions between control mortar bars and test mortar bars. Both kinds of mortar bars are made by certain graded Pyrex glass and high-alkali cement, except 25 percent of cement by volume is replaced by pozzolan in the test mortar bars. A suitable pozzolan should have a minimum of 75 percent reduction in 14-day mortar bar expansion.

Fly ash

Although the chemical compositions of fly ashes vary in a wide range, they generally consist of large amounts of silica, and lower amounts of aluminum, and iron oxides with varying amounts of calcium, magnesium, titanium and alkali oxides. The

preventive effects of fly ash on the deleterious alkali-aggregate reaction depend on the constitution of fly ash itself. It has been reported that some fly ashes act as an inert diluent with respect to alkalis in concrete [30, 67, 105]. Fly ashes used in these studies can be classified as Class F (low-calcium) fly ashes according to ASTM C 618 [2]. However, other reports show that expansion could be reduced to different levels by replacement of cement with fly ash even the alkali contents are kept constant in the mortar bars [47]. Thus, fly ash does not simply act as an inert diluent with respect to alkalis in mortar.

Fly ash replacement in concrete does not always reduce the expansion caused by alkali-aggregate reaction. It may show a pessimum effect in expansion. For a fly ash with a high alkali content, small replacements by fly ash may produce an increase in expansion, but expansion can be reduced by replacement with larger amounts of fly ash [40, 47, 66, 68, 106]. In studies of pore solutions carried out by Diamond and Lopez-Flores [33] and Diamond [31], the alkali and hydroxyl concentrations can be reduced by addition of Class F (low-calcium) fly ashes, but addition of Class C (high-calcium) fly ashes will increase these concentration. Dunstan [40] suggested a minimum percentage of fly ash replacement to reduce the expansion caused by alkali-aggregate reaction, approximately equal to the percentage of calcium oxide content of the fly ash.

Consequently, deleterious effects of alkali-aggregate reaction can be reduced by sufficient replacement of fly ash, and the effectiveness of the replacement depends on the type and composition of fly ash.

Granulated blastfurnace slag

The use of granulated blastfurnace slag in concrete can effectively inhibit the deleterious expansion caused by alkali-aggregate reaction. It has been identified that the slag hydration products are essentially the same as those of portland cement, and the hydrated slag has a strong bonding effect on alkali and calcium ions [31, 92, 124, 151]. Sims [121] found that addition of slag to concrete has beneficial effect in expansion when the total alkali content in the mix is high, but has a less beneficial effect for low-alkali cement. Smolczyk [123] and Locher [89] reported that higher alkali content can be allowed in the mix when slag is used as a mineral admixture, 1.10% equivalent Na_2O for 50% slag replacement and 2.0% of equivalent Na_2O for 65% slag replacement. In many cases, 50 percent of slag replacement may effectively reduce the expansion [67, 106].

AVAILABLE ALKALIS IN FLY ASH

Experimental

Six common Iowa fly ashes and reagent grade calcium hydroxide were used in this research. X-ray diffraction analysis performed on a Siemens D-500 diffractometer showed that the reagent grade calcium hydroxide (obtained from Fisher Scientific Company) was pure and showed no carbonation. Sources, locations and classifications in accordance with ASTM C 618 of fly ashes are given in Table 3.

TABLE 3. Sources, locations and classifications of fly ashes

Fly Ash Generating Station	Abbreviation	Location	ASTM C 618-85 Classification
Clinton	CLI	Clinton, Ia.	F
Neal 2	NE2	Sioux City, Ia.	F
Lansing	LAN	Lansing, Ia.	C
Neal 4	NE4	Sioux City, Ia.	C
Ottumwa	OTT	Ottumwa, Ia.	C
Council Bluffs	CBF	Council Bluffs, Ia.	C

Elemental compositions of six Iowa fly ashes were

determined by flame photometry and quantitative X-ray fluorescence spectrometry performed with a Siemens LC-200 sequential spectrometer using methods described in detail in earlier publications [102, 119], and their results are given in Table 4. Sodium content of the Class C fly ashes were. higher than those of Class F fly ashes but the opposite was true for potassium contents. The total equivalent alkalis (% eq. Na_2O = % Na_2O + 0.658 x % K_2O), however, ranged from 1.36% to 2.72% without showing a trend with the ash classification.

The available alkalis of six Iowa fly ashes were studied as outlined by the procedures listed in ASTM C 311 [2]. The mixtures of 5g fly ash, 2g calcium hydroxide and 10ml deionized water were uniformly mixed and sealed in plastic vials. For comparing the alkali dissolution rates at different temperatures, the mixtures were cured at 38°C (as specified in ASTM C 311) and 55°C for varying lengths of time ranging from 2 days to 6 months. The available alkalis (solubilized alkalis) were extracted from the reaction products by mixing with water, filtering and washing with hot water. After the filtered solution has been neutralized by diluted HCl (1ml. concentrated HCl:3ml. H_2O) using phenolphthalein solution as the indicator, 5 ml of the same diluted HCl in excess was added into the filtered solution to acidify the filtrate. Quantitative analyses of the alkali contents (sodium and potassium) in the acidified filtrates were determined by a Backman DU-2 flame

TABLE 4. Elemental composition of fly ashes

	Class F		Class C			
	CLI	NE2	LAN	NE4	OTT	CBF
SiO_2	57.7	49.8	39.1	33.2	32.6	31.1
Al_2O_3	20.3	19.9	15.7	15.9	17.8	17.1
Fe_2O_3	14.8	9.0	5.4	5.6	5.2	5.3
MgO	1.3	3.5	5.6	5.4	4.4	5.8
CaO	5.9	13.2	26.0	25.1	24.0	26.9
TiO_2	1.0	0.8	1.3	1.1	1.4	1.4
SO_3	1.8	2.3	5.2	5.5	2.3	2.9
P_2O_5	0.0	0.5	0.7	0.9	1.8	1.2
K_2O	2.30	1.71	0.51	0.35	0.38	0.32
Na_2O	1.02	0.23	1.57	2.56	2.43	2.19
Total equivalent alkalis	2.53	1.36	1.91	2.79	2.68	2.40
Available alkalis at 28 days	0.77	0.34	1.13	1.44	1.68	1.46
% loss on ignition	1.25	0.35	0.13	0.32	0.23	0.57

photometer with an oxygen-hydrogen flame using procedures described in ASTM C 114 and C 311 [2]. Concentrations of Na_2O and K_2O were calculated separately using calibration equations, given in Table 5, determined by second degree regressions of the transmittance readings and the corresponding alkali

concentration. It was checked by dilution of solutions
containing some calcium and various concentrations of sodium
that the presence of calcium in the filtrates had negligible
influence on determination of Na_2O concentration.

TABLE 5.   Calibration equations for Na_2O and K_2O in the
           range of 0 to 100 ppm performed by Beckman DU-2
           flame photometer

Type of Alkalis	Calibration Equation
Na_2O	$C = 1.0253 + 0.2831T + 0.0070T^2$ $R^2 = 0.9989$ Standard error = 1.2508
K_2O	$C = 0.6579 + 0.8194T + 0.0017T^2$ $R^2 = 0.9996$ Standard error = 0.7134
	C = Concentration.
	T = Transmittance reading.

Presentation and Discussion of Results

The available alkalis in fly ash are the alkalis which can
be mobilized from fly ash into the liquid phase during the
reaction between fly ash and calcium hydroxide in the presence
of water. Available alkali content of fly ash can be expressed
either as the percent equivalent Na_2O (% eq. Na_2O) by weight of
fly ash or as the percentage of total equivalent alkalis in fly

ash. The term 'concentration of available alkalis' is used
when the available alkali content is expressed as % eq. Na_2O by
weight of fly ash, and 'amount of available alkalis' is used
when it is expressed as the percentage of total equivalent
alkalis in fly ash.

Figure 6 and Figure 7 show the measured concentration of
available alkalis in each fly ash when cured at 38°C and 55°C
for different periods of time. When cured at 38°C similar
trends were displayed by both types of ashes. Alkali
dissolution rates increased significantly with curing time
after passing a dormant period, but the rates slowed down after
about 40 days of curing. Table 4 lists the available alkali
content in each fly ash measured in accordance with ASTM C 311
(cured at 38°C for 28 days). According to ASTM C 618, only OTT
fly ash exceeded the maximum limit for available alkalis (1.5%
eq. Na_2O) when the fly ash is to be used as a mineral admixture
in Portland cement concrete containing reactive aggregates.
However, Figure 6 shows a large quantity of alkalis present in
both types of fly ashes mobilized into liquid phase
continuously after 28 days of curing at 38°C. The
concentration of available alkalis for all Class C fly ashes
exceeded the maximum limit of 1.5% eq. Na_2O after 5 to 6 months
curing at 38°C.

To study the percentage of total equivalent alkalis which
mobilized into liquid phase in these experiments, the
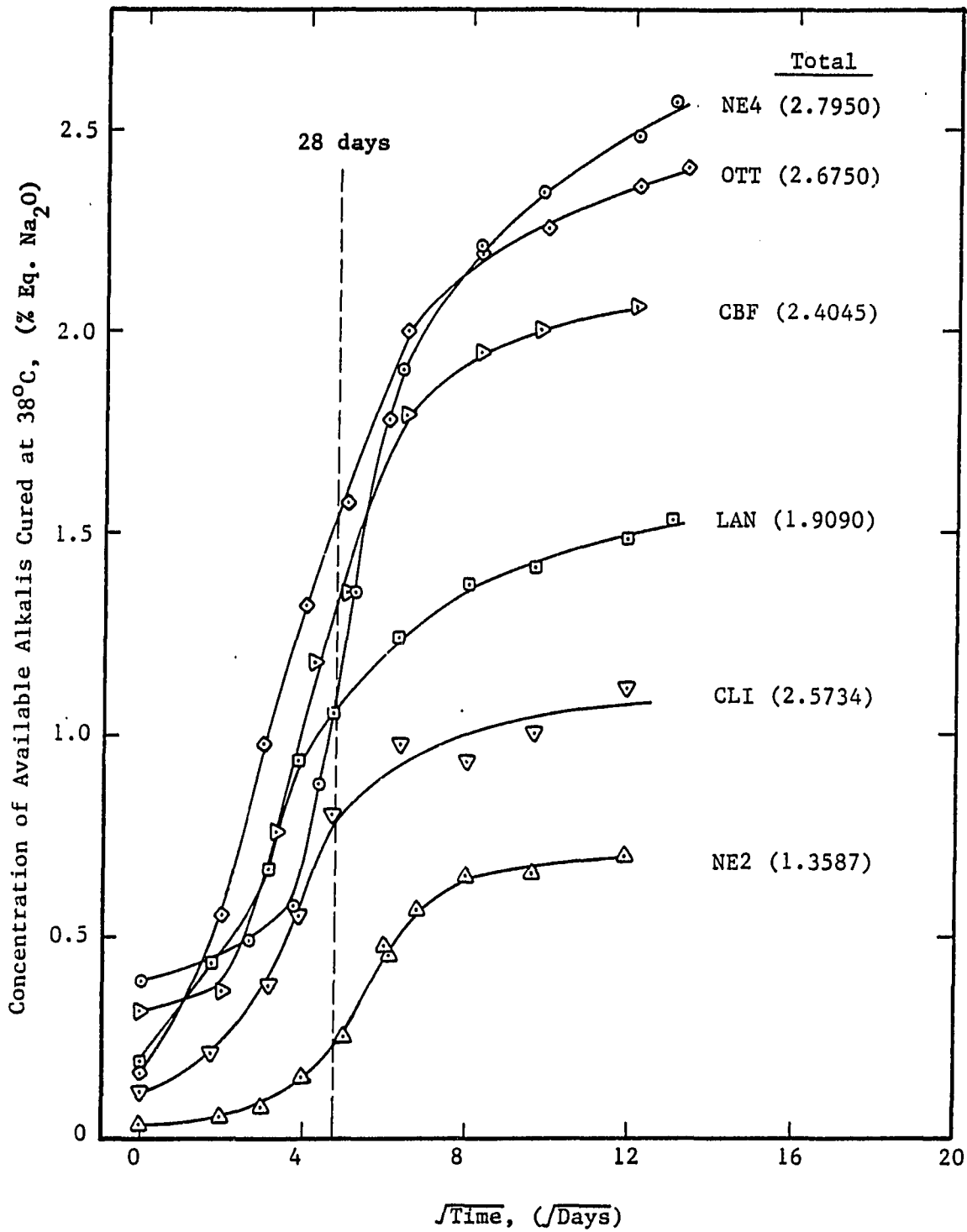
FIGURE 6. Concentration of available alkalis, %
equivalent Na_2O, when cured at 38°C
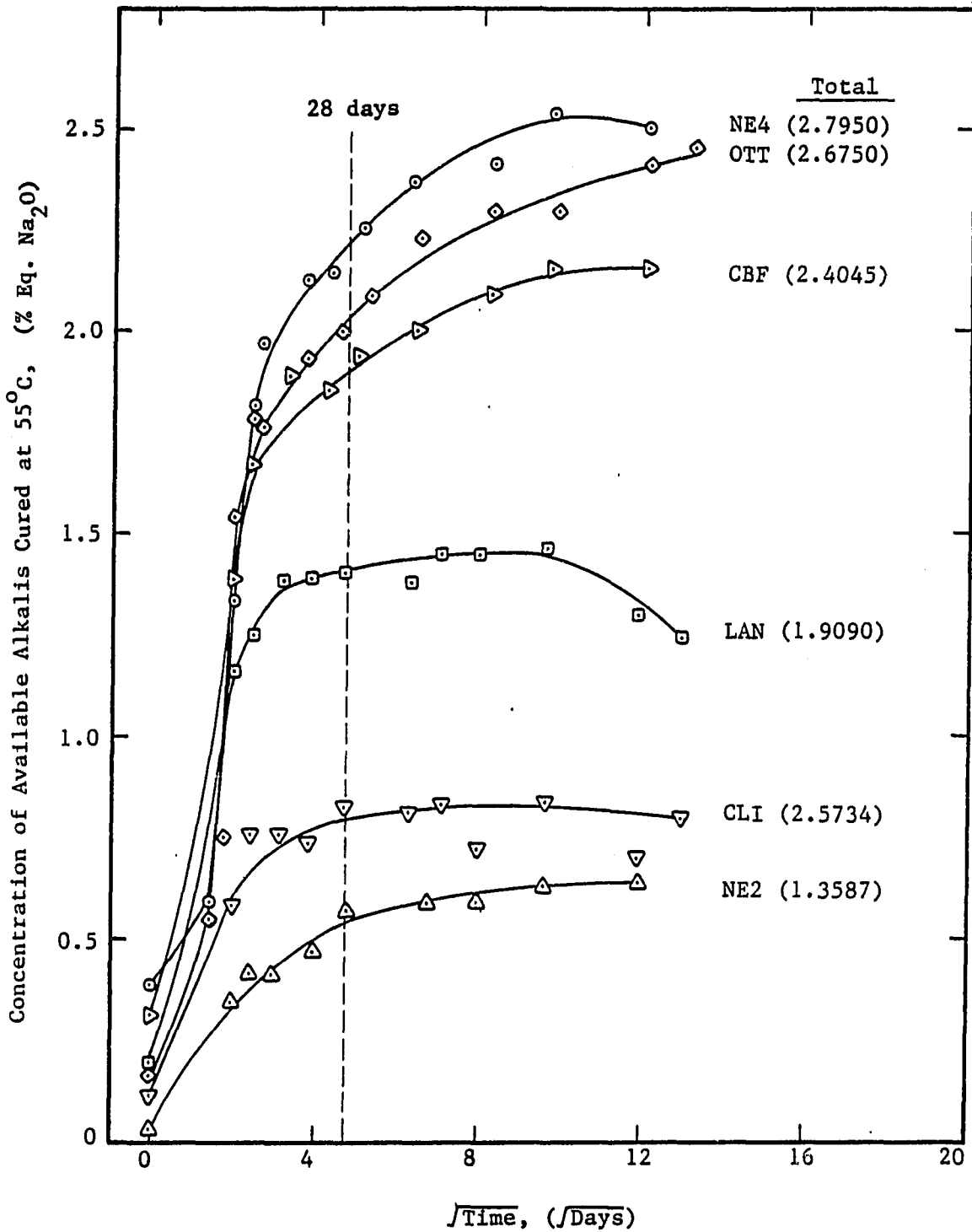
FIGURE 7. Concentration of available alkalis, %
equivalent Na_2O, when cured at 55°C

concentration of available alkalis in each fly ash, shown in Figures 6 and 7, were divided by the total equivalent alkalis contained in the corresponding fly ash to give normalized amount of available alkalis. Figures 8 through 13 show the normalized plots of the effects of temperatures and curing ages on the amount of available alkalis. The amount of available alkalis mobilized in these experiments approached about 50% of total equivalent alkalis for Class F fly ashes (Figures 8 and 9) and about 90% of total equivalent alkalis for Class C fly ashes (Figures 10 through 13) after 5 to 6 months of curing at 38°C. The amount of available alkalis was about 30% of total equivalent alkalis for Class F fly ashes and about 55% of total equivalent alkalis for Class C fly ashes when measured at 28 days of curing at 38°C (i.e., as specified in ASTM C 311). It is apparent that the Class C fly ashes tend to mobilize a much larger percentage of the total equivalent alkalis than the Class F fly ashes.

Available Alkali Mobilization at 38°C

The shapes of the 38°C alkali mobilization curves shown in Figures 6 and 8 through 13 illustrate that the 28-day available alkali test may be considered as a good indication of the long term release of alkalis into the liquid phase only for the Clinton fly ash (a strong Class F fly ash). The curves for all other fly ashes are still steeply inclined after 28 days of curing and hence, the test is not indicative of the total
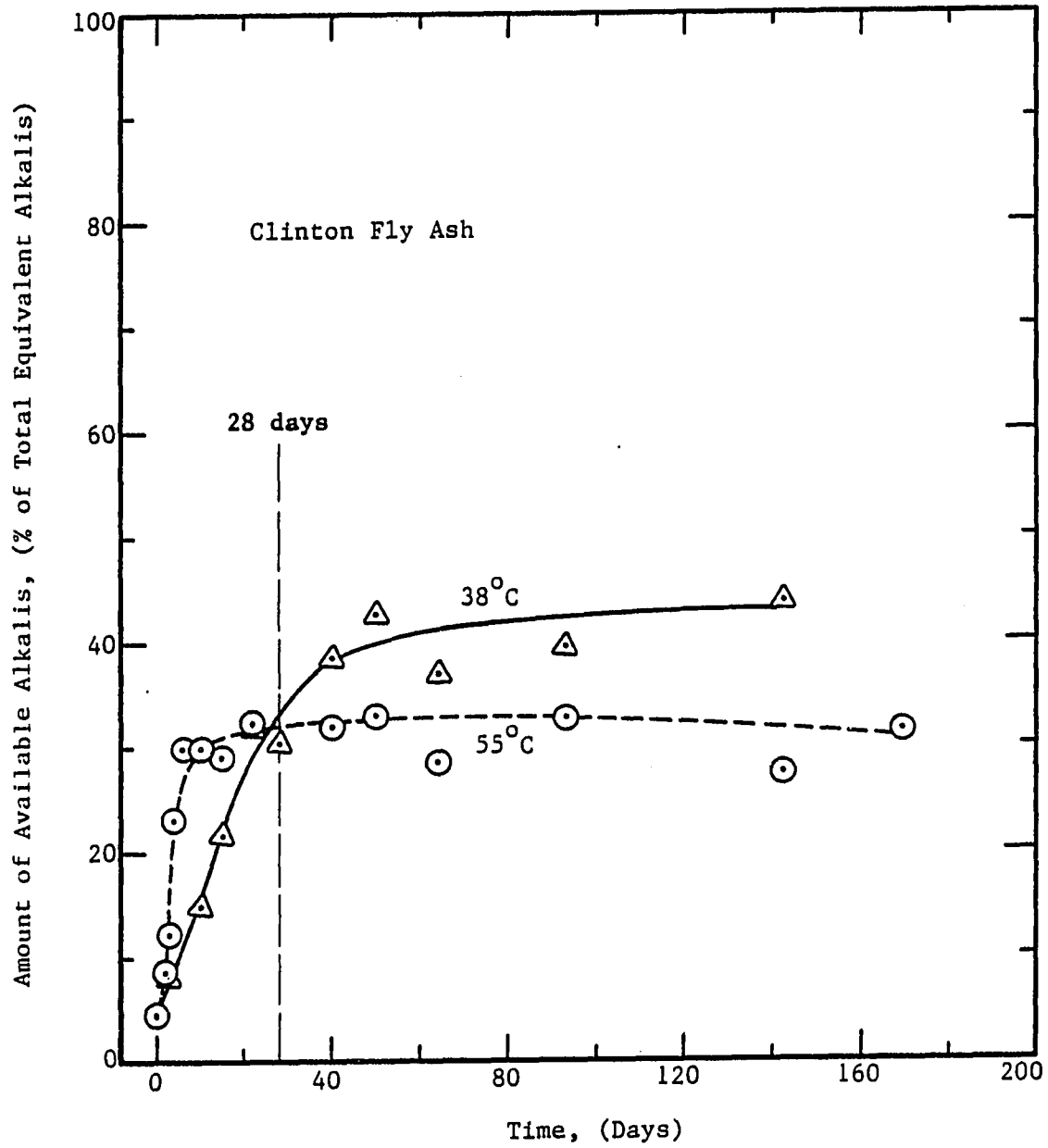
FIGURE 8. Effect of temperature on the mobilization of
available alkalis for Clinton fly ash
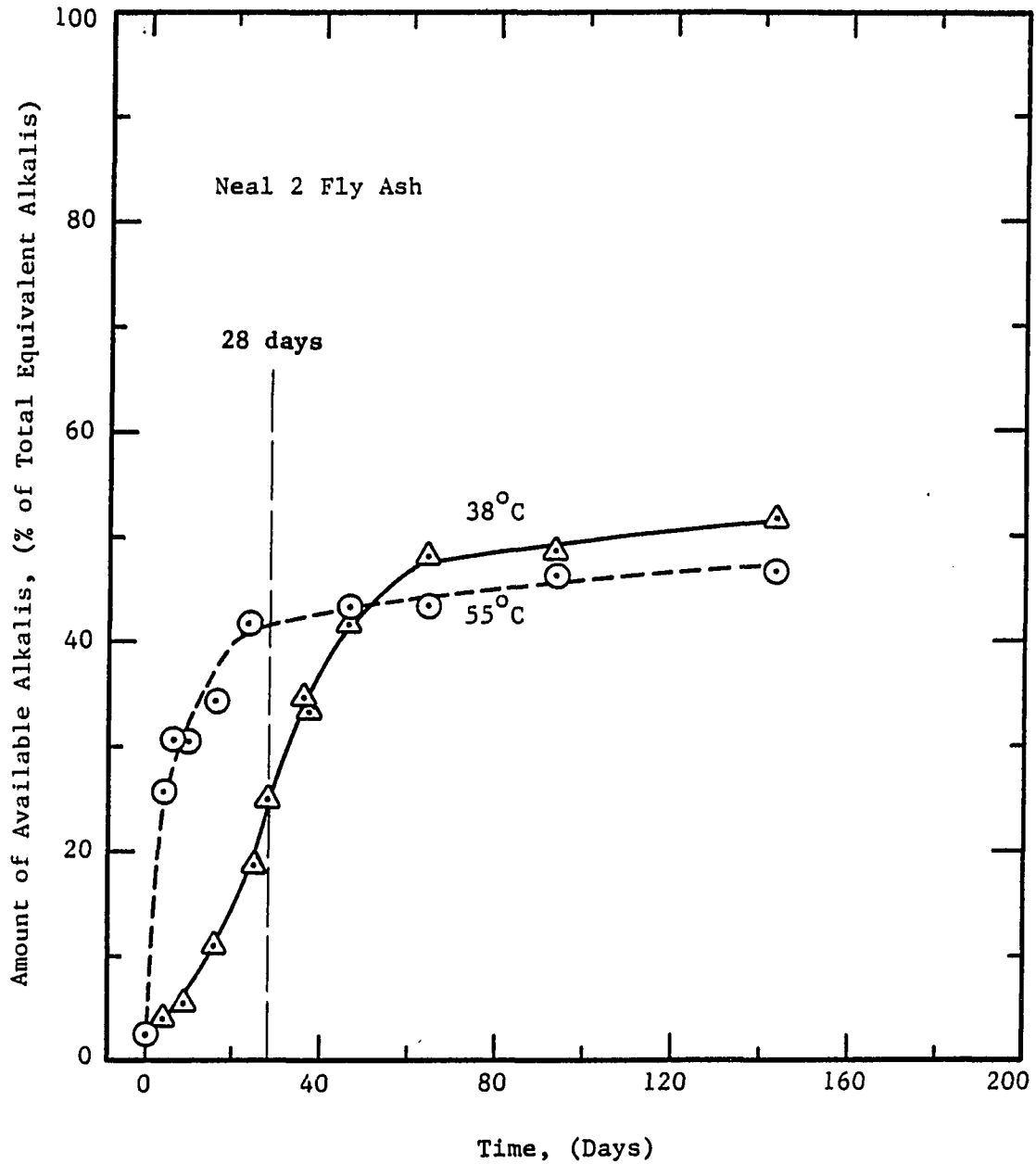
FIGURE 9. Effect of temperature on the mobilization of
available alkalis for Neal 2 fly ash
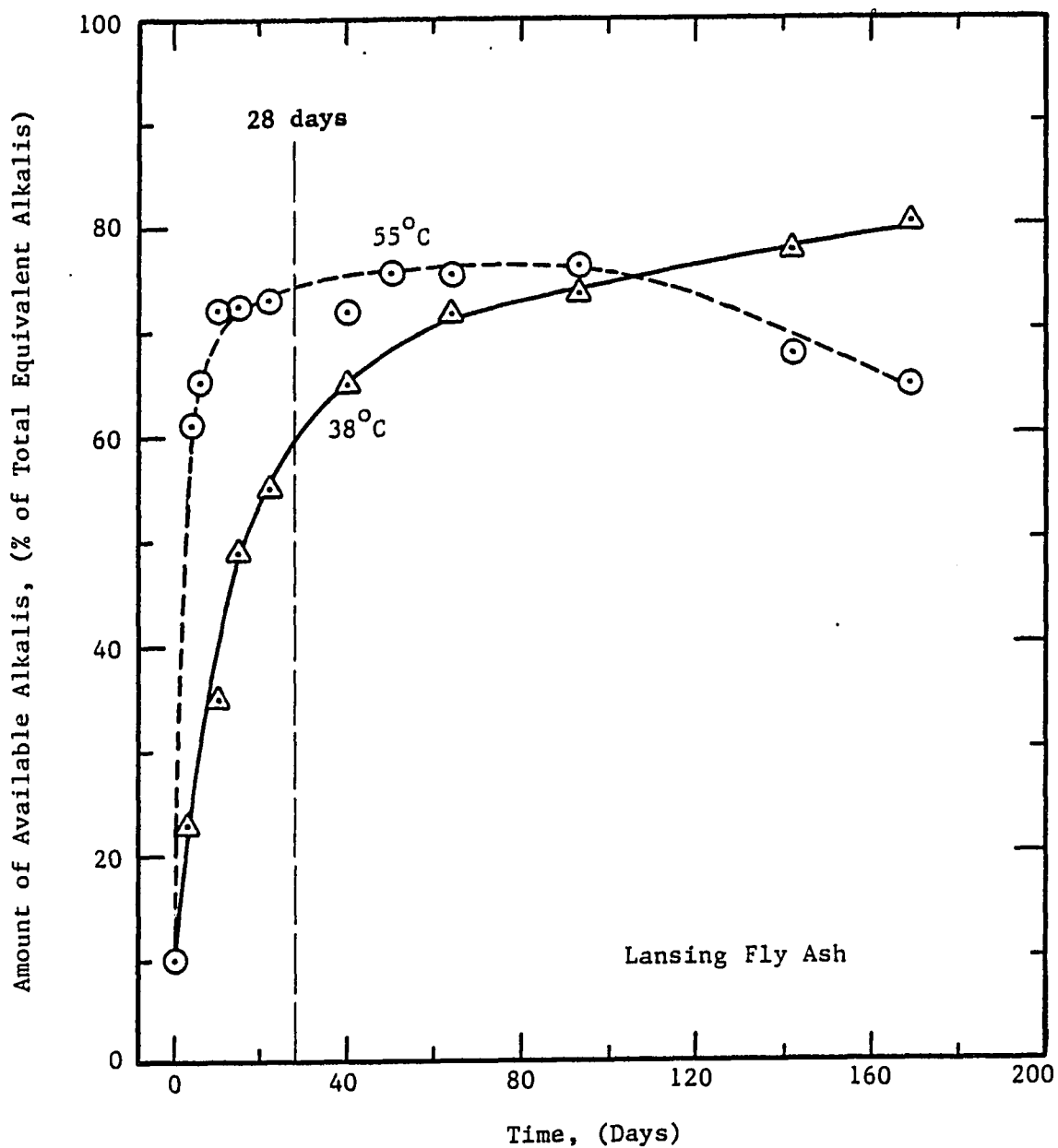
FIGURE 10. Effect of temperature on the mobilization of available alkalis for Lansing fly ash
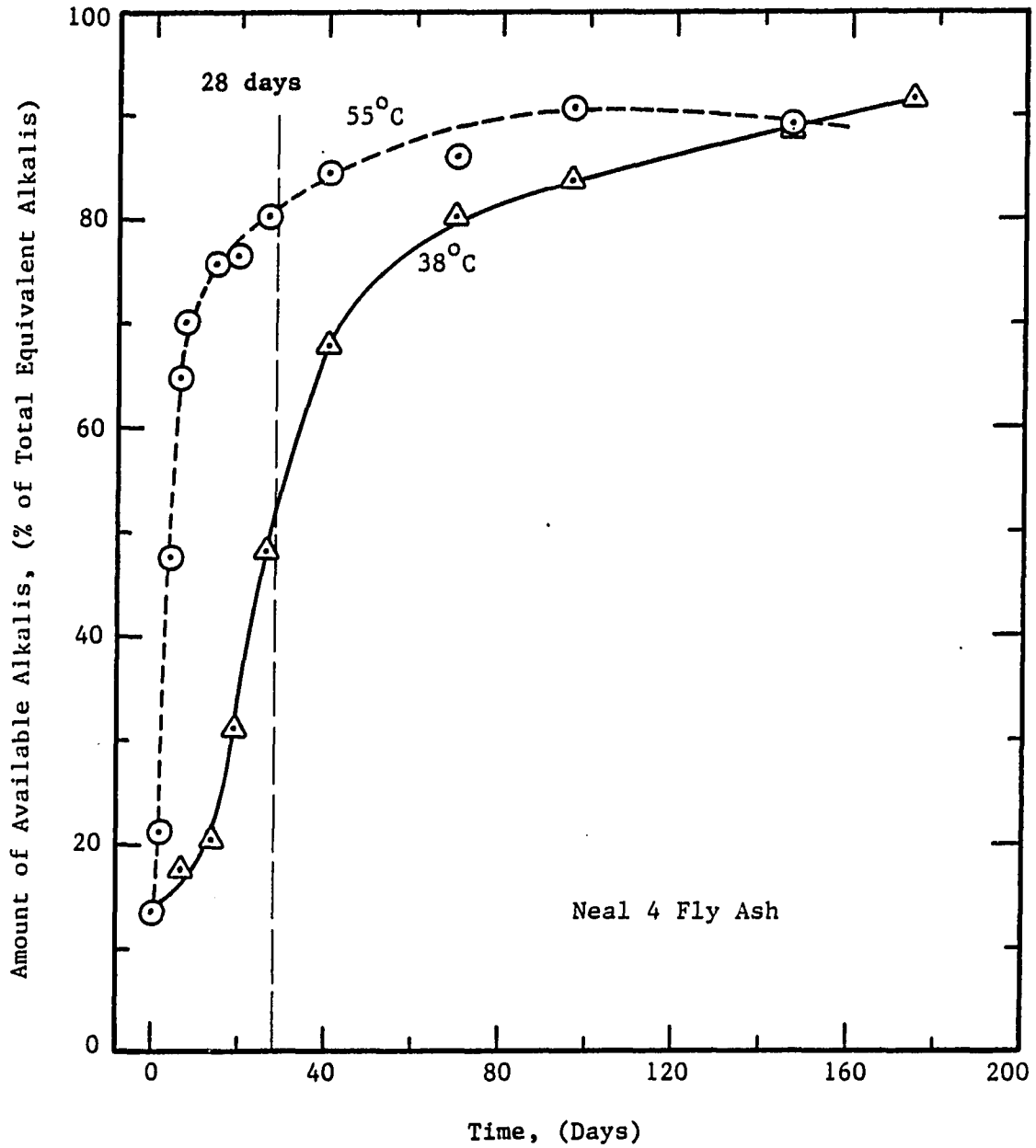
FIGURE 11. Effect of temperature on the mobilization of available alkalis for Neal 4 fly ash
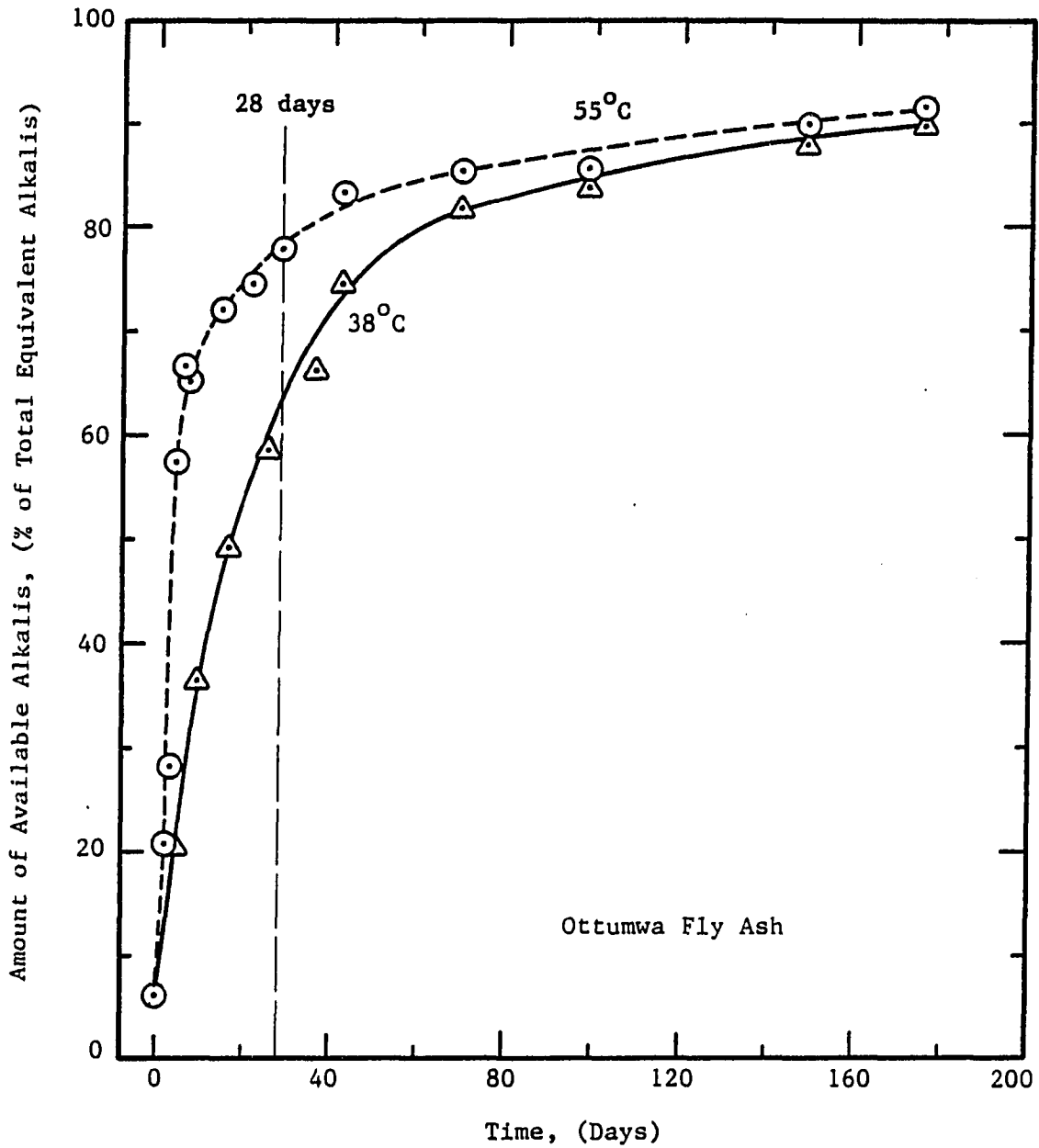
FIGURE 12. Effect of temperature on the mobilization of available alkalis for Ottumwa fly ash
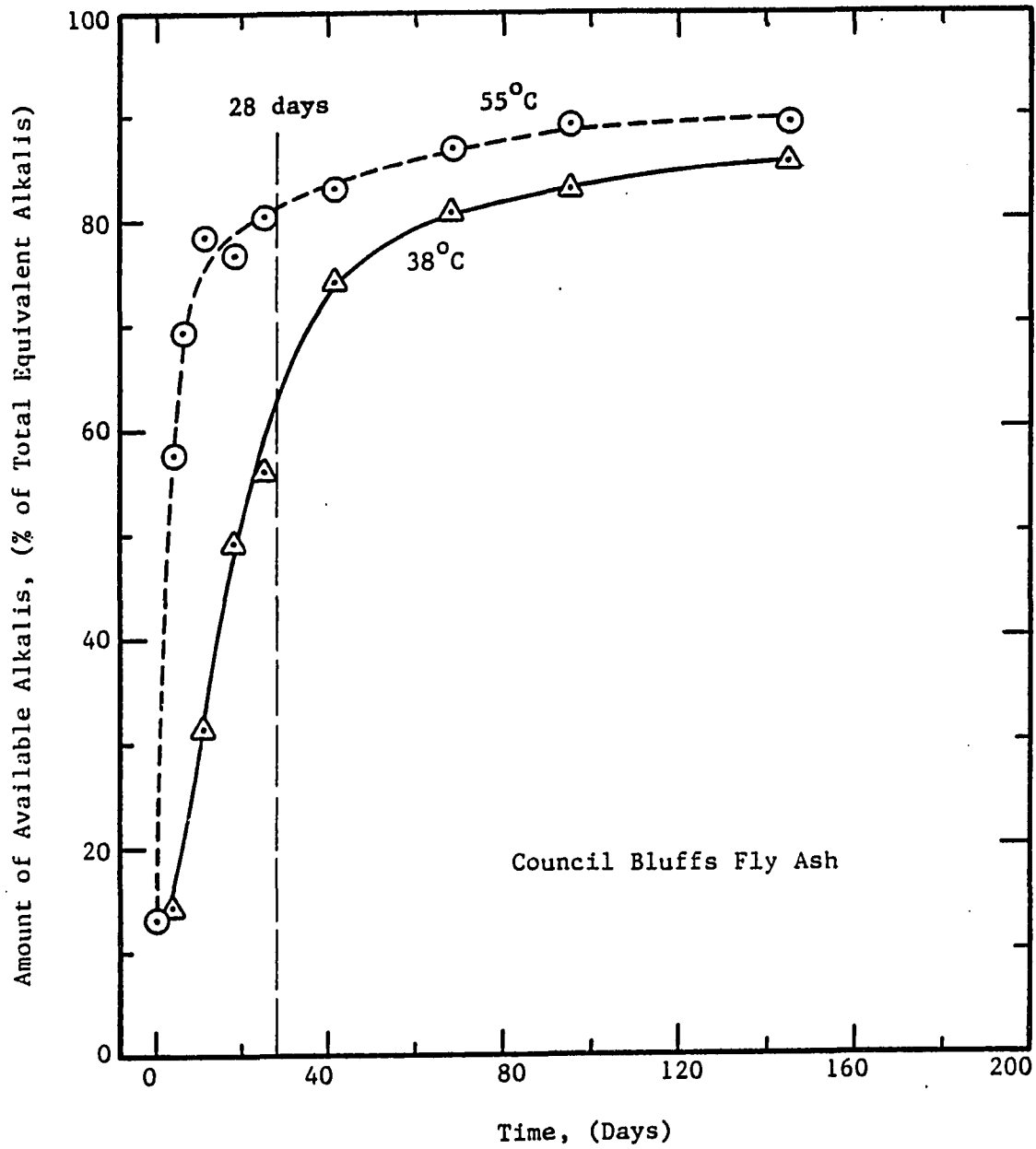
FIGURE 13. Effect of temperature on the mobilization of available alkalis for Council Bluffs fly ash

amount of alkalis that can be released into the liquid phase after long periods of time. The results obtained from these experiments seemed puzzling because the available alkali test has been used for many years as a standard method for assessing fly ash quality. However, a recent article published by Buttler, Morgan and Walker [17] shed some light on why this drastic difference exists between the amount of alkalis extracted from different fly ashes. Their experiments consisted of reacting three different pulverized fuel ashes (pfa - an abbreviation used in Britain for fly ash which is generally strongly Class F in character) with varying mass ratio of calcium hydroxide. They followed the concentration of alkalis released from the pfa as a function of time by using the analytical method described in ASTM C 311. The results of their experiments were as follows [17]:

1. the rate and amount of extraction of sodium and potassium ions increase as mass ratio, $pfa:Ca(OH)_2$, decreases

2. provided the mass ratio, $pfa:Ca(OH)_2$, is low all of the sodium and potassium ions present in the fly ash would ultimately be extracted

3. for the ASTM C 311 mass ratio of 5g pfa:2g $Ca(OH)_2$ there is little change in the amount of sodium and potassium ions extracted if the pastes are stored at 38°C for periods longer than 28 days.

In light of these results, and the data shown in Figures 6 through 13, it can be deduced that the available alkali test may not be valid for fly ashes containing large amounts of

calcium because the calcium (if reactive) could potentially

change the effective fly ash:calcium hydroxide ratio from its

assigned value of 2.5:1, an error which would cause more

alkalis to be mobilized. Thus, we may be dealing with an

additional (unspecified) variable when analyzing fly ashes with

high calcium contents. Quick calculations indicate that for

fly ash-calcium hydroxide pastes prepared using the six Iowa

fly ashes (chemical compositions are listed in Table 4) the

actual fly ash:calcium hydroxide ratios range from about 2:1 to

less than 0.9:1 when it is assumed that 100% of the calcium

present in the fly ash has the potential to react.

To study the relationships between the mobilization of

alkalis and the compositions of the reacting system (5g fly ash

+ 2g calcium hydroxide), Table 6 lists the calculated total

equivalent alkalis to silica, N/S, lime to silica, C/S, and

lime to acidic oxides (SiO_2, Al_2O_3 and Fe_2O_3), C/(S+A+F), mole

ratios in the reacting system by converting added calcium

hydroxide to the equivalent calcium oxide. The amount and the

concentration of ultimate available alkalis and the alkali

dissolution rates for each fly ash cured at 38°C are also given

in Table 6. Figure 14 shows that the concentration of ultimate

available alkalis, expressed as % eq. Na_2O, is strongly related

to the N/S mole ratio in the reacting system. The

concentration of ultimate available alkalis increases about

linearly with the N/S mole ratio in the reacting system. It is

interesting to note that the data point corresponding to Clinton fly ash which contained relatively high alkali and silica contents but low calcium content fits very well to this linear relationship. This suggests that the silica content in fly ash plays an important role in mobilization of alkalis.

Figures 15 and 16 indicate that the ultimate amount of available alkalis, expressed as the percentage of total equivalent alkalis, is controlled by the C/S or the C/(S+A+F) mole ratio in the reacting system. The amount of ultimate available alkalis was found to increase when the C/S or the C/(S+A+F) mole ratio in the reacting system was increased. This suggests that a larger amount of alkalis tends to be retained in the hydration products when the reacting system contains lower calcium but higher silica concentrations. Therefore, it can be inferred that the concentration and the amount of ultimate available alkalis in fly ash may be interrelated to the total alkali, silica and calcium contents in the reacting system in which alkali and silica contents determine the concentration of ultimate available alkalis, and calcium content controls the reactivity of the fly ash.

Alkalis in fly ash are supposed to exist in the form of sulfates or in the form of solid solution with silica or aluminate glass. The alkalis in the form of sulfates tend to dissolve rapidly into the liquid phase to give a measure of water soluble alkalis. Figure 17 shows that the concentration

TABLE 6. Mole ratios of oxides in the reacting system,
ultimate available alkalis and alkali dissolution
rates at 38°C

	Class F		Class C			
	CLI	NE2	LAN	NE4	OTT	CBF
Mole Ratios of Oxides in the Reacting System:						
Na_2O/SiO_2	0.0424	0.0267	0.0473	0.0813	0.0796	0.0747
CaO/SiO_2	0.6718	0.9448	1.5421	1.7871	1.7838	1.9698
$CaO/(SiO_2+Al_2O_3+Fe_2O_3)$						
	0.5154	0.7179	1.1972	1.3286	1.2916	1.4196
Ultimate Available Alkalis at 38°C:						
% equivalent Na_2O by weight of fly ash						
	1.1098	0.7014	1.5341	2.5676	2.4030	2.0594
% of total equivalent alkalis						
	43.13	51.62	80.36	91.86	89.83	85.65
Alkali Dissolution Rates at 38°C:						
% equivalent Na_2O per square root of days						
	0.1776	0.1312	0.2157	0.4099	0.3044	0.3269
% of total equivalent alkalis per square root of days						
	6.9004	9.6604	11.3003	14.6661	11.3791	13.7574

and the amount of water soluble alkalis are somewhat related to
the sulfate content in the fly ash. However, it can not be
simply concluded that the sulfate content in fly ash controls
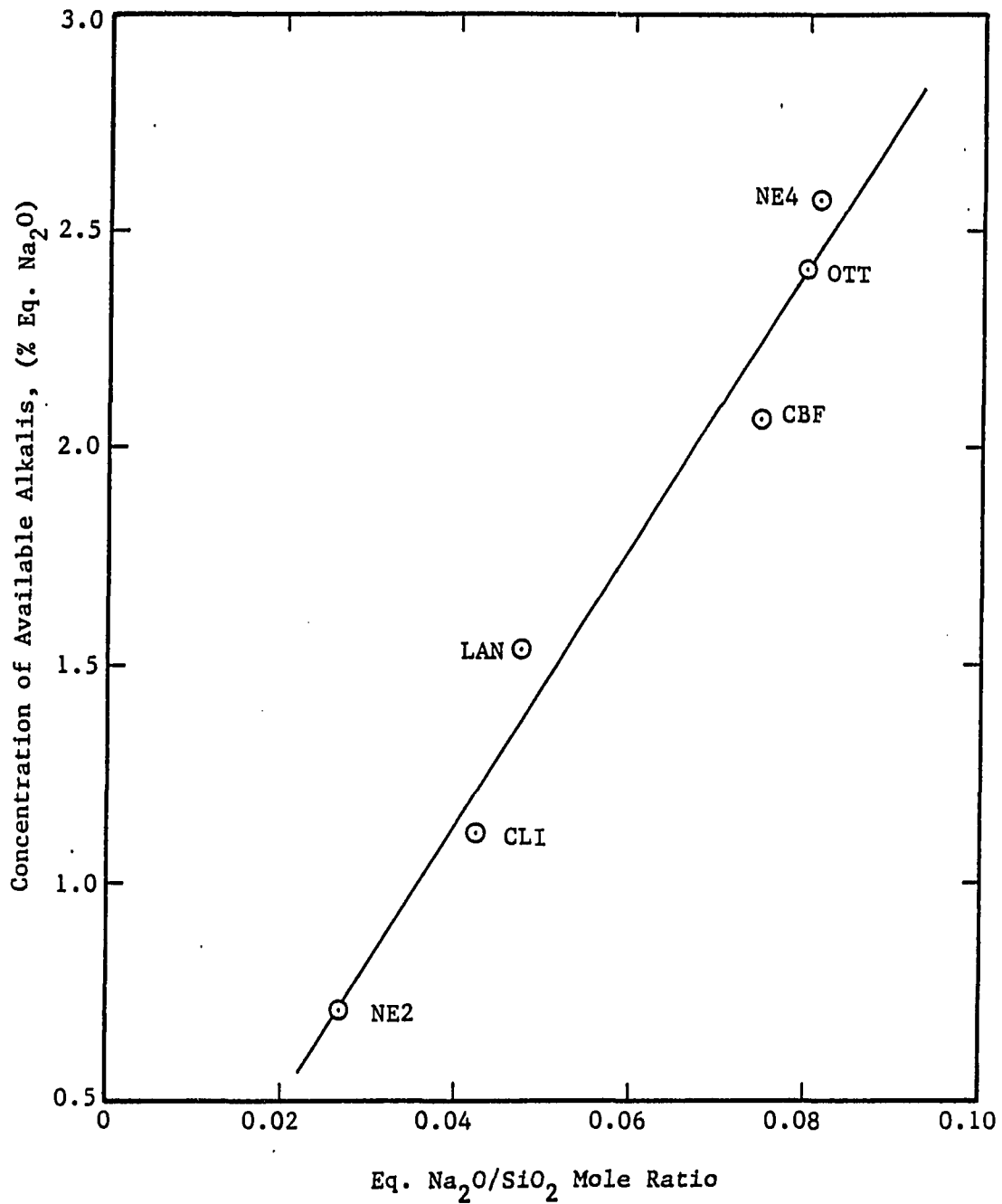
FIGURE 14. Relationship between concentration of ultimate available alkalis and alkali to silica mole ratio in the reacting system
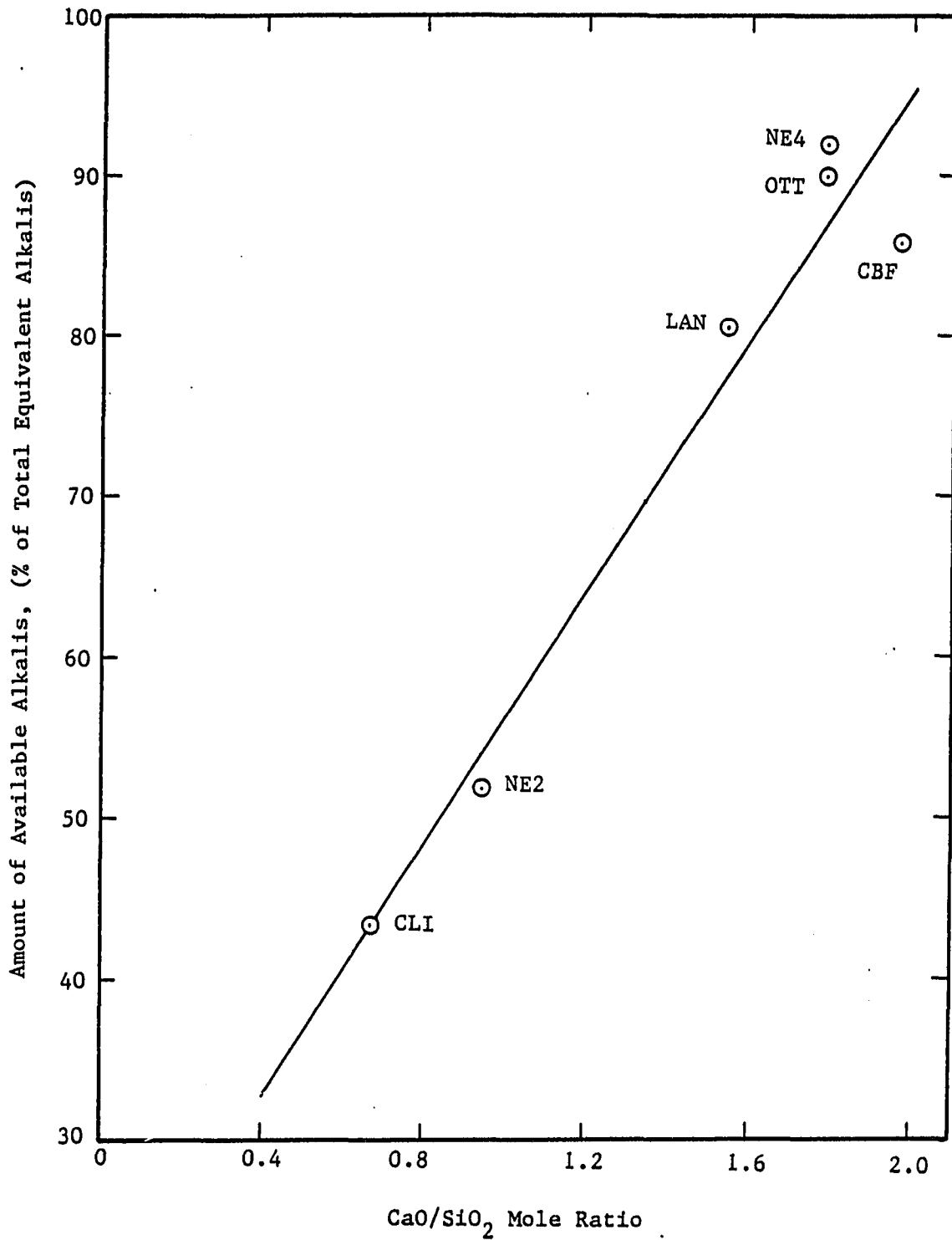
FIGURE 15. Relationship between amount of ultimate available alkalis and lime to silica mole ratio in the reacting system
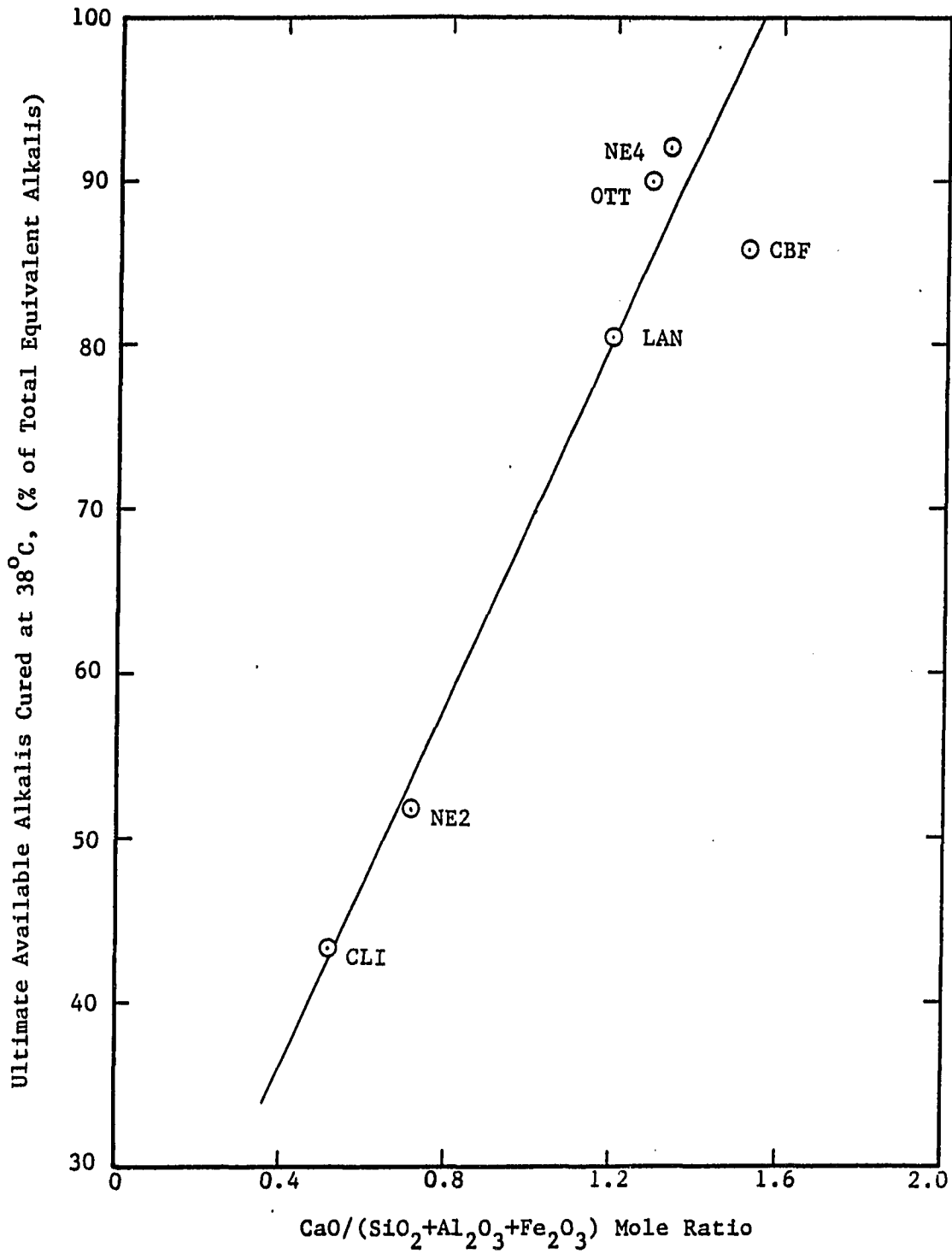
FIGURE 16. Relationship between amount of ultimate available alkalis and lime to acidic oxides mole ratio in the reacting system

the concentration and the amount of water soluble alkalis because the sulfate combines not only with alkali ions but also with other cations, such as calcium ions, in fly ash.

When fly ash reacts with calcium hydroxide in the presence of water, the calcium ions react with silica and aluminate glasses in fly ash to form hydration products similar to the products from cement hydration. During formation of hydration products, silica and aluminate glasses are supposed to preferentially combine with calcium ions. When the reacting system contains low calcium and high silica concentrations (low C/S mole ratio), calcium cations are not sufficient to react with silica and aluminate glasses forming stable hydration products. At this time, alkali ions tend to be retained in the structure of hydration products neutralizing the charge deficiencies. When the reacting system contains high C/S mole ratio, the calcium concentration is sufficient to react with silica and aluminate glasses forming stable hydration products. Thus, alkali cations tend to mobilize into the liquid phase increasing the risk of deleterious alkali-silica reaction in concrete. In this study, more than 85% of total equivalent alkalis mobilized into the liquid phase when the C/S or C/(S+A+F) mole ratio was greater than 1.75 or 1.3, respectively. Based on this alkali mobilization hypothesis, it can be inferred that the amount of ultimate available alkalis would be increased by increasing calcium or decreasing silica
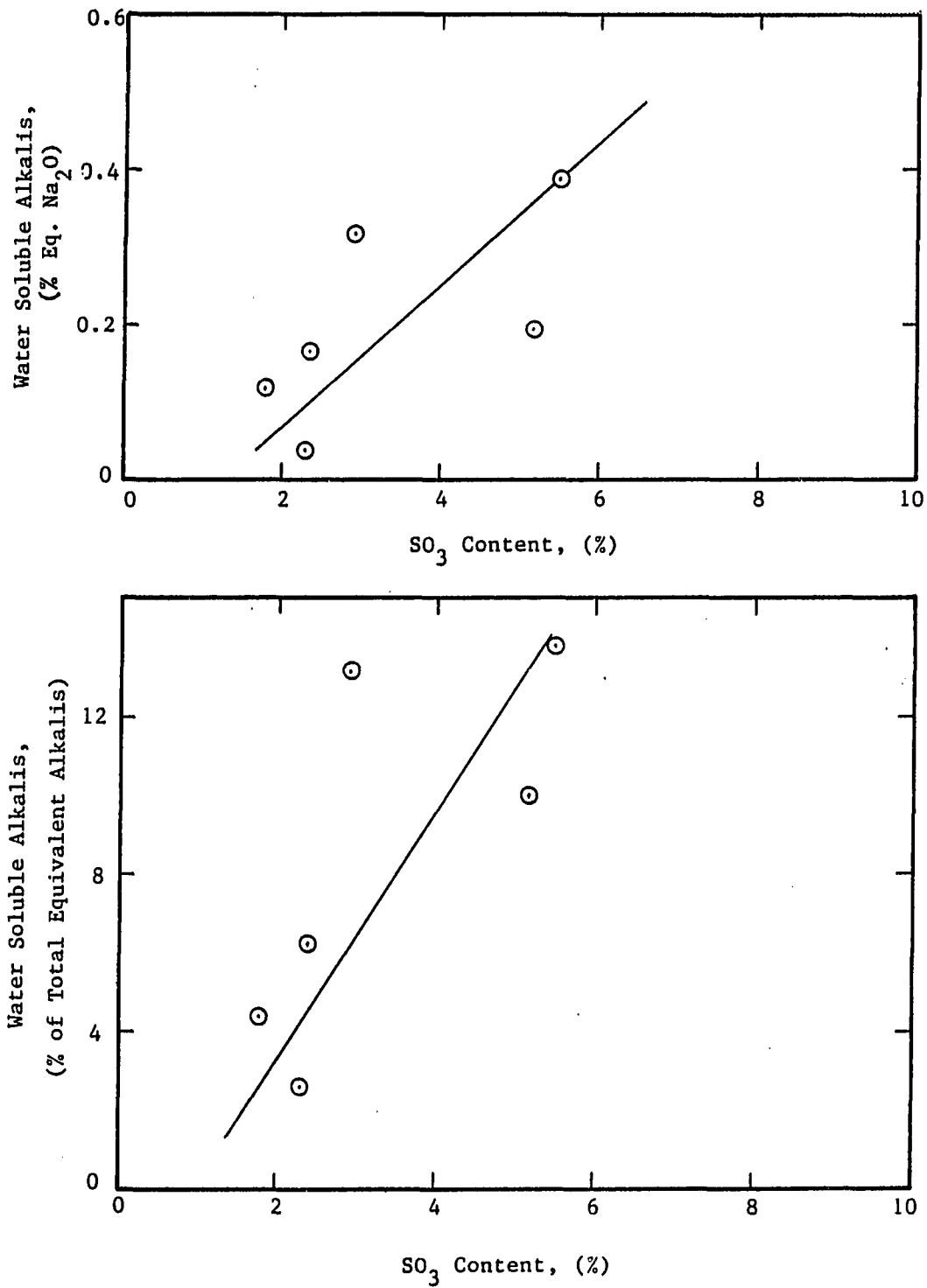
FIGURE 17. Relationship between water soluble alkalis and sulfate content in fly ash

contents in the reacting system which is supported by Buttler et al.'s [17] decreasing pfa:Ca(OH)$_2$ mass ratio studies.

If the above alkali mobilization hypothesis is true, the concentration of ultimate available alkalis is not only related to the alkali contents but also related to the silica content in the reacting system. For a given calcium concentration in the reacting system, the silica glass tends to have the ability to retain a certain amount of alkalis in its hydration products. The higher the silica content in the reacting system, the greater the tendency of alkalis to be retained in the hydration products. When the reacting system contains high N/S mole ratio, high alkali but low silica contents, the concentration of alkalis is too high to be retained in low silica content hydration products. For a reacting system with low N/S mole ratio, silica content is high enough to retain part of alkalis in its hydration products to give less ultimate available alkali concentrations. For example, Clinton fly ash with lower N/S mole ratio gave less concentration of ultimate available alkalis than those of Class C fly ashes with higher N/S mole ratio. However, the concentration of ultimate available alkalis should be also related to the calcium concentration in the reacting system. The influence of calcium content and its effects on the relationships between the concentration of ultimate available alkalis and the N/S mole ratio are not clear from these experiments.

Investigations of alkali mobilization curves, shown in
Figures 6 through 13, indicate that alkalis dissolve rapidly
and about linearly to the square root time scale after a
dormant period up to about 40 days. Beyond 40 days of curing,
alkali dissolution rates slowed down and became less time
dependent. The slope of the linear portion of alkali
dissolution curve is considered to be the alkali dissolution
rate as listed in Table 6. It is interesting to find that the
alkali dissolution rate was again related to the compositions
of the reacting system. Figure 18 shows that the rate of
available alkali dissolution, % equivalent Na_2O per square root
of days, increases with increasing the N/S mole ratio in the
reacting system. This indicates that the concentration of
available alkalis in the liquid phase increases faster when the
reacting system contains higher alkali and lower silica
contents because insufficient amount of silica is available to
retain alkalis, and relatively low silica content reacts faster
with a given amount of calcium content.

Figure 19 and Figure 20 indicate that the alkali
dissolution rates, expressed as the percentage of total
equivalent alkalis per square root of days, were increased when
the C/S or the C/(S+A+F) mole ratio in the reacting system was
increased. This suggests that the alkali dissolution rates
tend to increase when either the fly ash itself or the reacting
system contains large amount of calcium as compared with silica
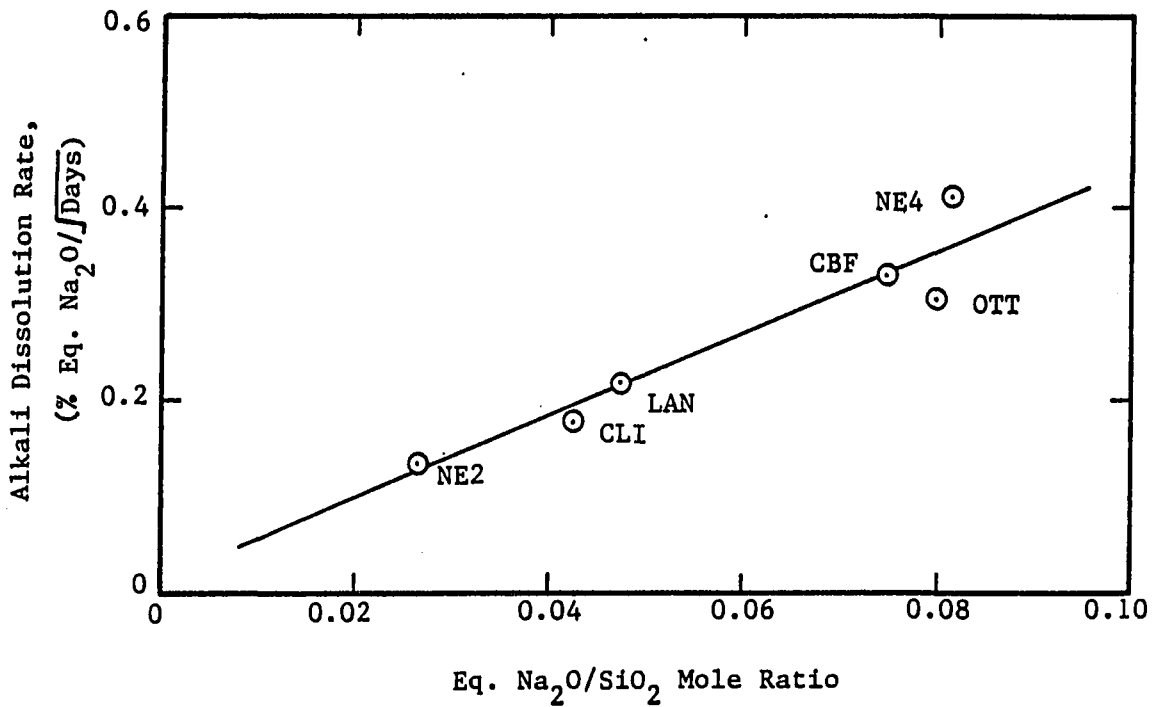
FIGURE 18. Alkali dissolution rates vs. N/S mole ratio

content.

Consequently, the available alkalis in fly ash depend not only on the curing ages but also on the compositions in the reacting system in which alkali, silica and calcium contents are major variables. In summary, the concentration and the rate of concentration increase of available alkalis seem to be increased with increasing the N/S mole ratio in the reacting system, and the amount and the rate of alkali mobilization tend to be controlled by the C/S mole ratio in the reacting system. Thus, the silica content in the reacting system appears to determine the amount of alkalis which can be retained in the hydration products. The calcium content in the reacting system

Alkali Dissolution Rate,

(% of Total Eq. Alkalis/$\sqrt{Days}$)

CaO/SiO$_2$ Mole Ratio

⊙ CLI NE2 ⊙ LAN ⊙ OTT ⊙ NE4 ⊙ CBF ⊙
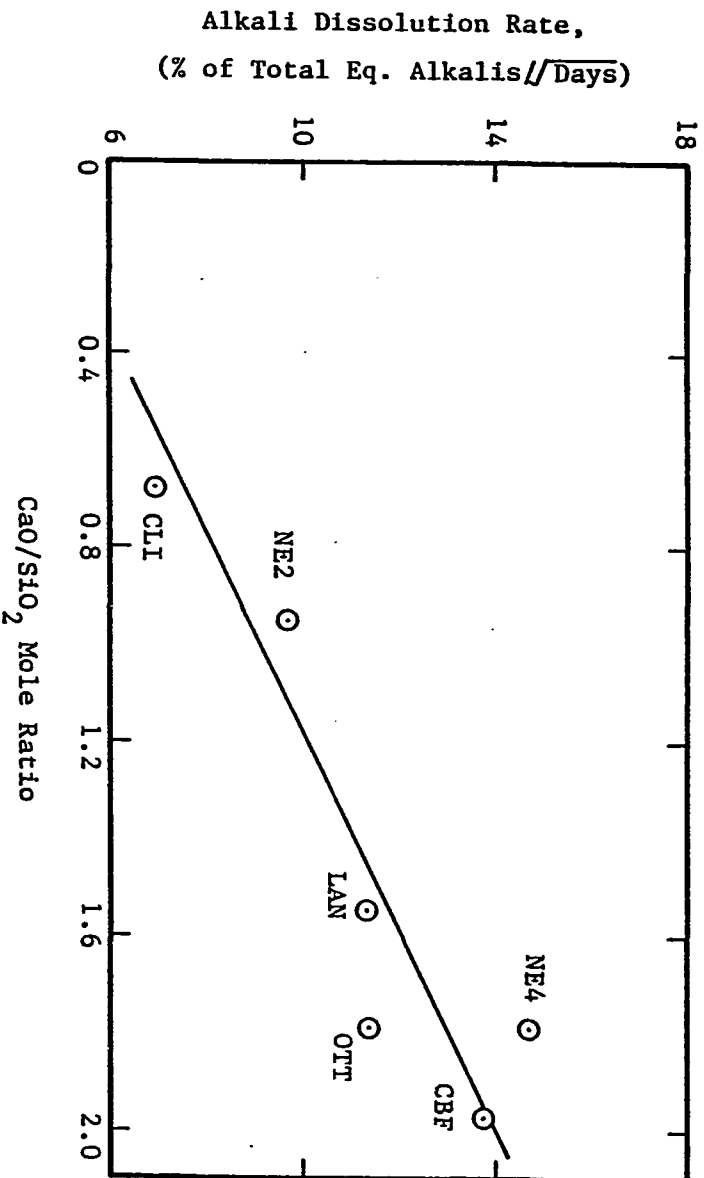
FIGURE 19.   Alkali dissolution rates vs. C/S mole ratio

Alkali Dissolution Rate,

(% of Total Eq. Alkalis/$\sqrt{Days}$)

CaO/(SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$) Mole Ratio

⊙ CLI NE2 ⊙ LAN ⊙ OTT ⊙ NE4 ⊙ CBF ⊙
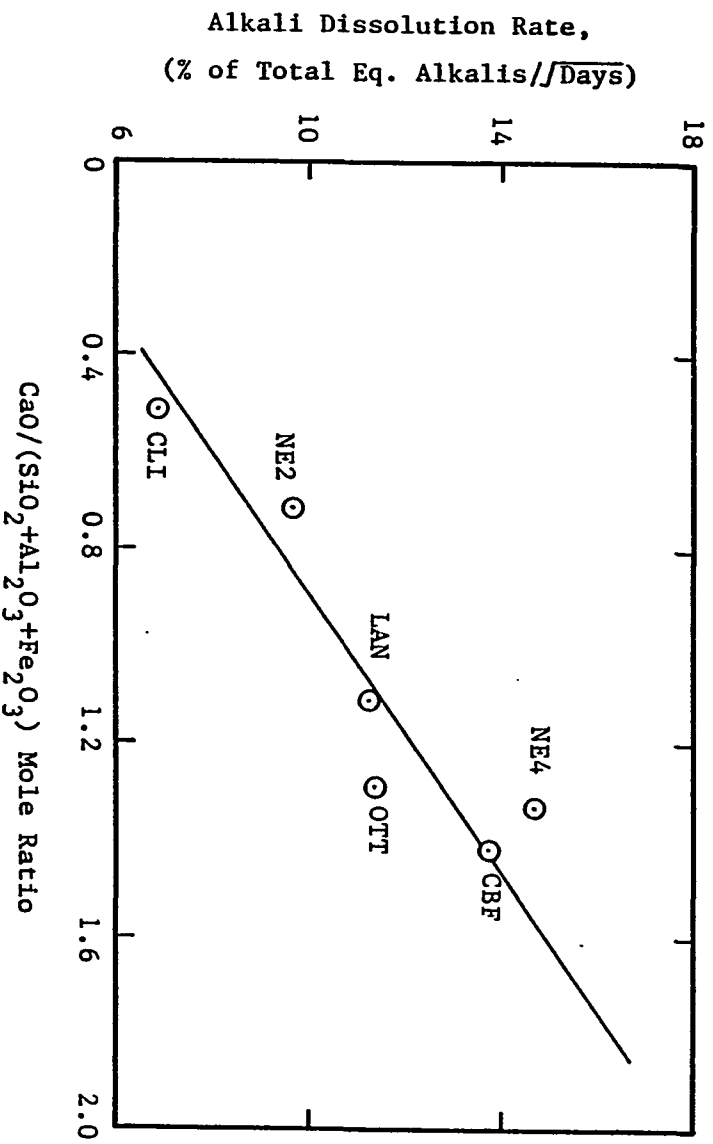
FIGURE 20.   Alkali dissolution rates vs. C/(S+A+F) mole ratio

may influence the reactivity of fly ash. Though the acidic oxide contents ($SiO_2+Al_2O_3+Fe_2O_3$) in the reacting system showed good relationship with the amount and the concentration of ultimate available alkalis, the individual effects of Al_2O_3 and Fe_2O_3 are still not clear because they are minor components in the fly ashes studied.

Available Alkali Mobilization at 55°C

To investigate the possibility of shortening the time required to complete the available alkali test, a modification was made by increasing the curing temperature to 55°C. Figures 7 through 13 present the results obtained from these experiments. As expected, the alkali dissolution rates were significantly increased for curing periods up to about 40 days. When cured for 7 days at 55°C, the available alkali contents were found to be more than 65% and about 30% of the total equivalent alkalis for Class C and Class F fly ashes, respectively. Their values are considerably higher than those obtained at 38°C by the standard ASTM method. Beyond 40 days of curing at 55°C, the alkali dissolution rates for the three Class C fly ashes, OTT, NE4 and CBF, approached the available alkalis obtained for the samples subjected to the 38°C curing and thus became less temperature dependent. A trend showing a decrease in available alkali content with increasing temperature was observed with two of the Class C ashes, LAN and NE4, and with both of the Class F fly ashes, CLI and NE2,

studied, as can be seen in Figures 8 through 11. With these four fly ashes the available alkali release curve at 38°C intercepts the 55°C curve, giving higher available alkali release at 38°C beyond the intersection of the two curves. The curing time at the intersection of the two curves, at which equal relative available alkalis are released from the fly ashes, appears to be inversely related to the SiO_2 content as shown in Figure 21. It is interesting to note that the remaining two Class C fly ashes (OTT and CBF) which do not behave in this manner have the least silica content.
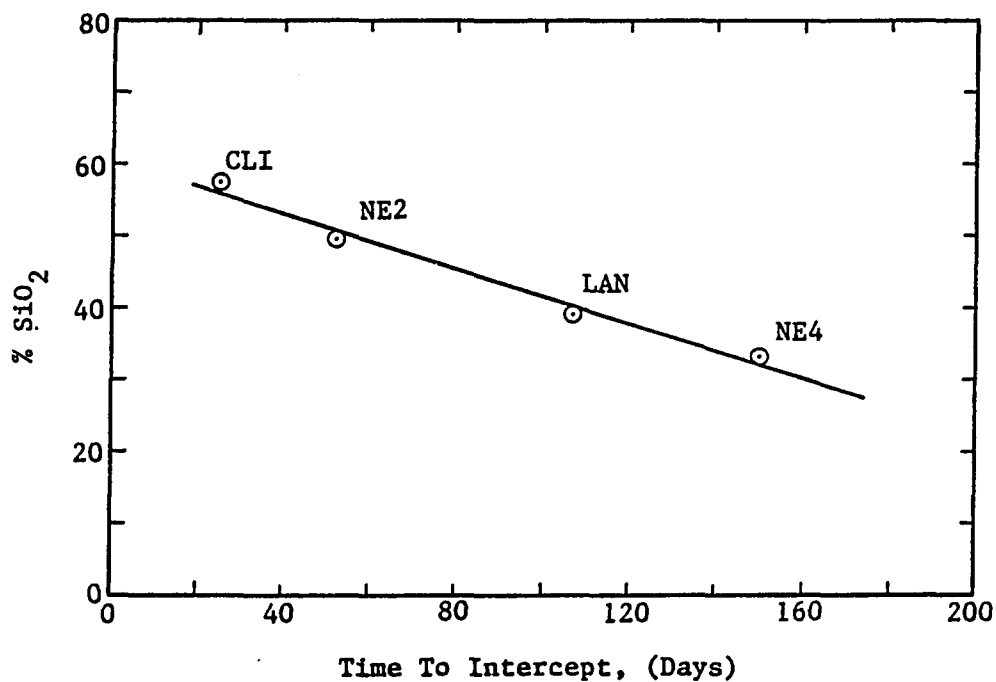
FIGURE 21. Relation between silica content and curing time for equal relative available alkalis release at curing temperature of 38°C and 55°C

The unique behavior observed during this phase of study appears contrary to the initial anticipation that temperature close to ambient levels would mainly influence the kinetics of the hydration and pozzolanic reactions and would have little or no influence on phase equilibria. Competing and successive reactions, however, might complicate the kinetics assumed to be controlled by only one category of components, namely alkalis. During the reaction between fly ash and calcium hydroxide in the presence of water, the hydration products of the fly ash with higher silica content tend to retain greater amounts of alkalis at 55°C than at 38°C. For example, an obvious decrease in available alkalis for LAN fly ash after about 100 days of curing at 55°C indicates that the released alkalis tended to recombine with the hydration products. It appears that silica, being an acidic oxide tend to consume as much of the available basic oxides as possible to form thermodynamically stable silicates. Evidently, at elevated temperatures the rate of consumption of basic oxides surpasses the rate of their release, the alkali release and consumption being two successive and competing reactions. A systematic investigation of this proposed mechanism is recommended for future studies.

The individual mobilization behavior of sodium and potassium cations rather than the combined equivalent alkalis, are shown in Figure 22. It shows the relationship between the percentage of extracted sodium and the percentage of extracted

potassium obtained from each experiment for both Class C and Class F fly ashes cured at 38°C and 55°C. Most of the data points are distributed slightly above a line with equal percentage of the extracted sodium and potassium. This indicates that the amount of extracted sodium is only slightly greater than that of the extracted potassium. Thus, it is reasonable to simplify the problem by assuming that sodium and potassium cations have similar ability to leave the fly ash particles.

Summary

Available alkalis in six Iowa fly ashes were studied in accordance with the procedures listed in ASTM C 311 [2]. Results obtained from these experiments indicate that ASTM standard method for available alkali test tends to underestimate the ultimate amount of alkalis that may be extracted from a fly ash-calcium hydroxide paste after long periods of curing at 38°C. The concentration of ultimate available alkalis, % equivalent Na_2O, and the rate of the concentration increase in the liquid phase tend to be increased when the total equivalent alkalis to silica mole ratio in the reacting system is increased. The amount of ultimate available alkalis, expressed as the percentage of total equivalent alkalis, and the alkali dissolution rates seem to increase with increasing lime to silica mole ratio in the reacting system.
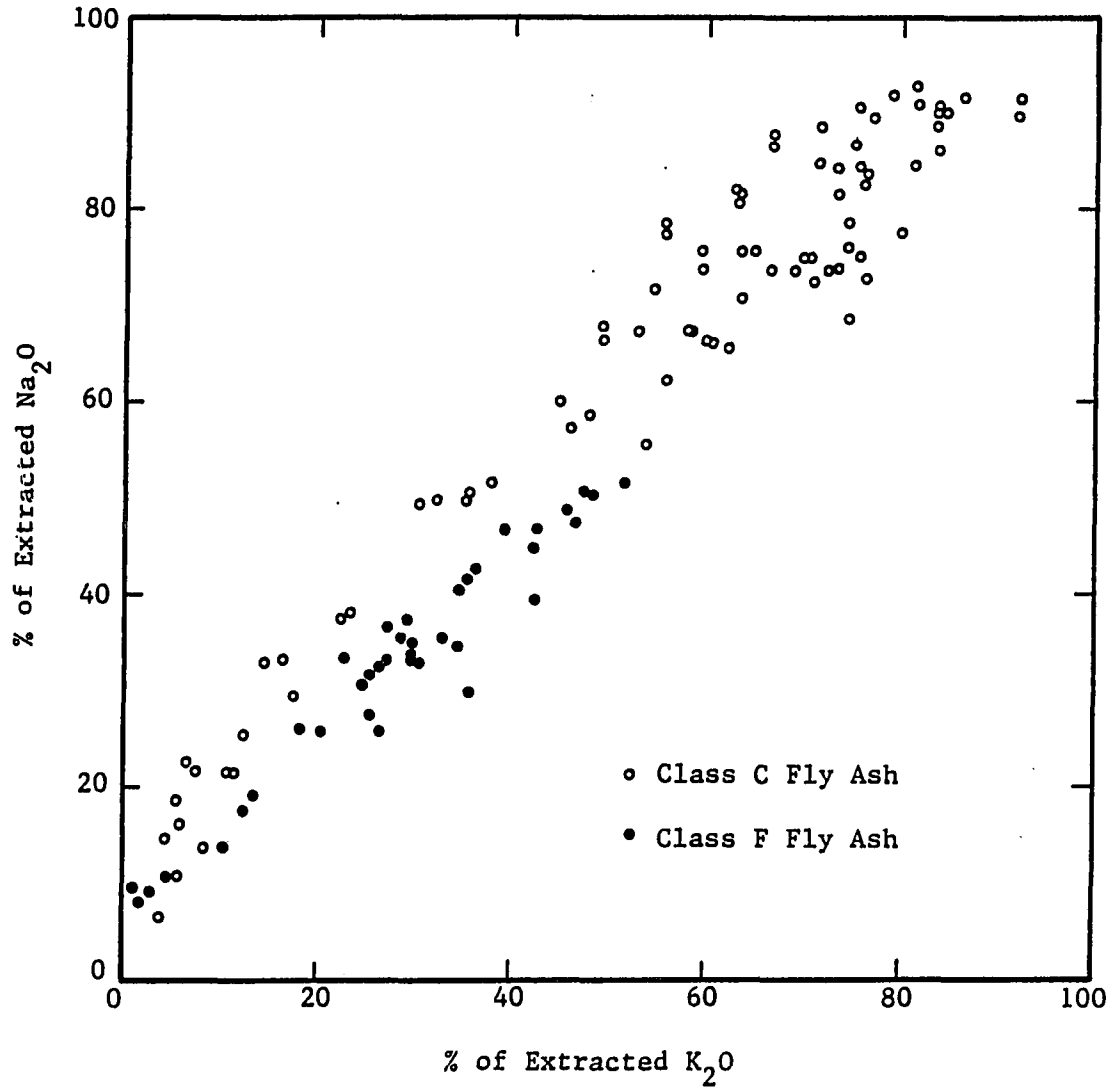
FIGURE 22. Relationship between the amount of extracted
sodium and potassium for equal curing period at
temperature of 38°C and 55°C

The silica content of the reacting system determines the amount
of alkalis that can be retained in the hydration products. The
calcium content of the reacting system influences the
reactivity of fly ash. Larger amounts of alkalis are retained
in the hydration products when the reacting system contains
higher silica but lower calcia contents. It is proposed that
the calcium content of fly ash causes a systematic error in the
standard procedure used for measuring available alkalis. An
increase of calcium content in fly ash itself or an increase of
calcium hydroxide in the reacting system tends to increase the
amount of ultimate available alkalis and their dissolution
rates.

For the majority of the fly ashes studied, an increase in
the curing temperature to 55°C resulted in a reduction in the
concentration of available alkalis after long periods of time.
The observed reduction in available alkalis of fly ash-calcium
hydroxide mixtures at elevated temperatures suggests that, at
present, increasing the curing temperature is not a suitable
way for decreasing the curing time required for the routine
available alkali test. However, tests conducted at elevated
temperatures are significant in research for fly ash
characterization.

No significant difference was found in the individual
dissolution behavior of sodium and potassium cations from fly
ash particles into the liquid phase.

EFFECTS OF ALKALIS IN FLY ASH ON ALKALI-SILICA REACTION

Experimental

In order to study the effects of alkalis in fly ash on alkali-silica reaction, two types of cements, a type I high-alkali cement and a type II low-alkali cement, and three Class C fly ashes with various alkali contents were used in mortar expansion tests. Sources, locations, abbreviations and classifications of the cements and fly ashes used are given in Table 7 and Table 8, respectively.

TABLE 7. Cement abbreviations, types and alkali contents used in mortar bar tests

Cement	Abbreviation	Type	Alkali Content
Davenport Cement	DAV	I	0.85
North Dakota Cement	ND	II	0.49

X-ray diffraction analyses indicated that both cements exhibited a certain degree of carbonation. The chemical compositions of cements and fly ashes were investigated using the equipment and the methods described previously. Results obtained are given in Table 9. Davenport cement was considered to be a high-alkali cement because its alkali content exceeded

TABLE 8. Fly ash sources, locations, and ASTM
         classifications used in mortar bar tests

Fly ash Generating Station	Abbreviation	Location	ASTM C 618 Classification
Ontario	ONT	Thunder Bay, Ontario	C
Ottumwa	OTT	Ottumwa, Iowa	C
Neal 4	NE4	Sioux City, Iowa	C

the 0.6% equivalent Na_2O maximum limit specified in ASTM C 150 [2], whereas North Dakota cement was a low-alkali cement. The available alkali contents, measured according to ASTM C 311, of three fly ashes were in the range of 1.46 to 3.42. Only NE4 fly ash met the requirements specified in ASTM C 618 [2] as a mineral admixture in concrete containing reactive aggregate.

Table 10 lists the calculated alkali, silica and calcium contents of the cement-fly ash pastes used in each mortar bar test.

Pyrex glass No. 7740 was used as the reactive aggregate in mortar bars. The glass rods obtained from Fisher Scientific Company were crushed, washed and graded in accordance with the requirements described in ASTM C 441 [2]. X-ray diffraction analysis showed that the glass consisted of pure amorphous materials and no crystalline compound.

TABLE 9.   Chemical composition of cements and fly ashes used
           in mortar bar tests

	Cement		Fly Ash		
	DAV	ND	ONT	OTT	NE4
CaO	63.25	64.33	13.10	24.25	27.19
SiO_2	21.84	22.17	40.70	31.55	33.29
Fe_2O_3	2.48	3.80	4.80	4.90	6.17
Al_2O_3	4.34	4.25	19.10	17.71	15.83
MgO	2.53	1.81	2.70	4.78	5.80
SO_3	2.27	2.39	1.49	3.18	3.76
TiO_2	0.25	0.21	0.99	1.35	1.03
P_2O_5	0.12	0.08	0.55	1.81	0.85
Na_2O	0.26	0.13	6.92	3.13	2.10
K_2O	0.89	0.55	0.69	0.40	0.25
Total Alkalis, % Eq. Na_2O	0.85	0.49	7.37	3.39	2.26
Available Alkalis, @ 28 days, % Eq. Na_2O	---	---	3.42	2.16	1.46
Specific Gravity	3.15	3.15	2.45	2.63	2.64

Two 1" X 1" X 11 1/4" mortar bars were made for each
mixture in accordance with the procedures described in ASTM
standard test method for effectiveness of mineral admixture in
preventing excessive expansion of concrete due to the alkali-
aggregate reaction (C 441) [2].   Both cements were mixed

TABLE 10. Chemical composition of cement-fly ash pastes
used in mortar tests

	Na_2O	K_2O	Eq. Na_2O	CaO	SiO_2
DAV-CONTROL	0.26	0.89	0.85	63.25	21.84
DAV-ONT-15%	1.06	0.87	1.63	57.20	24.12
DAV-ONT-25%	1.63	0.85	2.19	52.92	25.73
DAV-ONT-40%	2.53	0.82	3.08	46.12	28.28
DAV-OTT-15%	0.63	0.83	1.17	58.24	23.09
DAV-OTT-25%	0.89	0.78	1.40	54.75	23.96
DAV-OTT-40%	1.29	0.71	1.76	49.30	25.31
DAV-NE4-15%	0.50	0.81	1.03	58.61	23.33
DAV-NE4-25%	0.66	0.75	1.16	55.37	24.34
DAV-NE4-40%	0.92	0.66	1.35	50.32	25.94
ND-CONTROL	0.13	0.55	0.49	64.33	22.17
ND-ONT-15%	0.95	0.56	1.32	58.15	24.41
ND-ONT-25%	1.53	0.58	1.91	53.77	25.99
ND-ONT-40%	2.45	0.60	2.84	46.83	28.50
ND-OTT-15%	0.51	0.53	0.86	59.18	23.37
ND-OTT-25%	0.78	0.51	1.12	55.60	24.21
ND-OTT-40%	1.20	0.49	1.53	49.99	25.52
ND-NE4-15%	0.38	0.51	0.72	59.76	23.60
ND-NE4-25%	0.56	0.48	0.88	56.22	24.60
ND-NE4-40%	0.84	0.44	1.13	51.02	26.16

separately with all three fly ashes for 0, 15, 25 and 40
percent replacements by volume. The weight ratio of aggregate
to cementitious materials was 2.25. The water content in the
mixture was determined to produce a flow of between 100 and 115
as described in ASTM C 109 [2]. The mix proportions for each

set of mortar bar are given in Table 11.

After one day moisture curing at room temperature, mortar bars were stored in sealed Plexy glass containers maintained at 100% relative humidity at 38°C for periods up to about 3 months. Expansion readings were taken at room temperature by removal of sealed container from 38°C oven at least 16 hours before measuring. Expansion data used for analyses was the average of two mortar bar expansion readings.

Five gram samples of cement-fly ash pastes corresponding to the pastes of mortar bar test specimens were mixed with 10g deionized water and sealed in vials cured at 38°C for measuring the active alkali content of each paste. Active alkalis are defined as the alkalis which can be mobilized from cement-fly ash paste into liquid phase during hydration of the paste, and which are supposed to induce the alkali-silica reaction. Active alkalis of each paste were extracted with hot water and measured by flame photometry using the equipment and the methods described previously after 28 days and 3 months of curing at 38°C.

To study the reaction products of alkali-silica reaction, 5g of mortar samples were prepared with compositions corresponding to those of mortar bar specimens except the Pyrex glass aggregate was crushed to pass through No. 100 sieve. The mortars were then mixed with 10g of deionized water, sealed in vials and cured at 38°C for 7 and 28 days. Reaction product

TABLE 11.   Mix proportions of mortar bars

	Cement (g)	Fly Ash (g)	Water (g)	Flow No.
Box I				
DAV-CONTROL	266.7	----	161.0	119
DAV-ONT-15%	226.7	31.1	141.4	104
DAV-ONT-25%	200.0	51.9	136.2	102
DAV-ONT-40%	160.0	83.0	132.0	108
ND-CONTROL	266.7	----	168.0	118
ND-ONT-15%	226.7	31.1	148.9	102
ND-ONT-25%	200.0	51.9	140.8	101
ND-ONT-40%	160.0	83.0	136.2	102
Box II				
DAV-CONTROL	266.7	----	153.0	111
DAV-NE4-15%	226.7	33.5	140.0	100
DAV-NE4-25%	200.0	55.9	140.4	113
DAV-NE4-40%	160.0	89.4	132.0	101
ND-CONTROL	266.7	----	162.0	114
ND-NE4-15%	226.7	33.5	150.2	106
ND-NE4-25%	200.0	55.9	141.4	102
ND-NE4-40%	160.0	89.4	137.6	105
Box III				
DAV-CONTROL	266.7	----	152.0	102
DAV-OTT-15%	226.7	33.4	141.0	100
DAV-OTT-25%	200.0	55.7	138.1	99
DAV-OTT-40%	160.0	89.1	135.4	109
ND-CONTROL	266.7	----	160.3	110
ND-OTT-15%	226.7	33.4	152.0	101
ND-OTT-25%	200.0	55.7	143.1	100
ND-OTT-40%	160.0	89.1	140.4	102

evaluations for those mortar samples were conducted by step
scan X-ray diffraction using monochromatic copper K alpha
radiation at a 50 kv, 25 ma setting. Count time was two
seconds with a step size of 0.04 degrees. Selected broken
pieces of mortar bars were also examined using a JEOL-U3
Scanning Electron Microscope equipped with energy dispersive X-
ray analyzer for evaluation of reaction product morphology.
The samples to be examined were coated with approximately 300
angstorm of gold for eliminating, or at least minimizing
charging.

Effects of alkalis from external sources, such as de-icing
salts or sea water, on alkali-silica reaction were investigated
using saturated NaCl bath method. Selected mortar bars which
were cured at 38°C for 28 days in sealed containers were
immersed in saturated NaCl solutions in containers kept at 38°C
in an oven. Expansions of the specimens were measured at room
temperature by removal of containers from the 38°C oven at
least 16 hours before measurements.

Presentation and Discussion of Results

Replacement of a portion of Portland cement with fly ash
as a mineral admixture is not always an effective method for
reducing the expansion caused by alkali-aggregate reaction in
concrete. Figures 23, 24 and 25 show the mortar bar expansions
for mixtures containing DAV (high-alkali) cement with 15, 25

and 40 percent replacements of ONT, OTT and NE4 fly ashes, respectively, along with the control mixture when cured at 38°C for periods up to about 12 weeks. As can be seen from Figures 23, 24, 25 and 29 DAV-ONT mortars gave considerably lower expansions than those given by mortars prepared using the other fly ashes with DAV cement. Since the control sample was also included in this trend, it could not be attributed to the role played by ONT fly ash in mortars. This trend is attributed to two factors: (1) uncontrollable differences in conditions prevailing in the three sealed containers, each dedicated to mortars prepared with one fly ash, and (2) segregation of Pyrex glass observed with mortars prepared with ONT fly ash. Although these factors make the absolute significance of the mortar bar test questionable, they do not affect the significance of the test for comparing samples prepared as a single batch. Compared to the control mixture, expansions were reduced by replacement of DAV cement with 40 percent of all three fly ashes and with 25 percent of OTT and NE4 fly ashes. Replacement of DAV cement with 15 percent of all three fly ashes and 25 percent of ONT fly ash exhibited greater expansions than the control mixture. Fifteen percent replacement of all three fly ashes produced the highest expansion which was considered to be the pessimum content of fly ash for DAV cement.
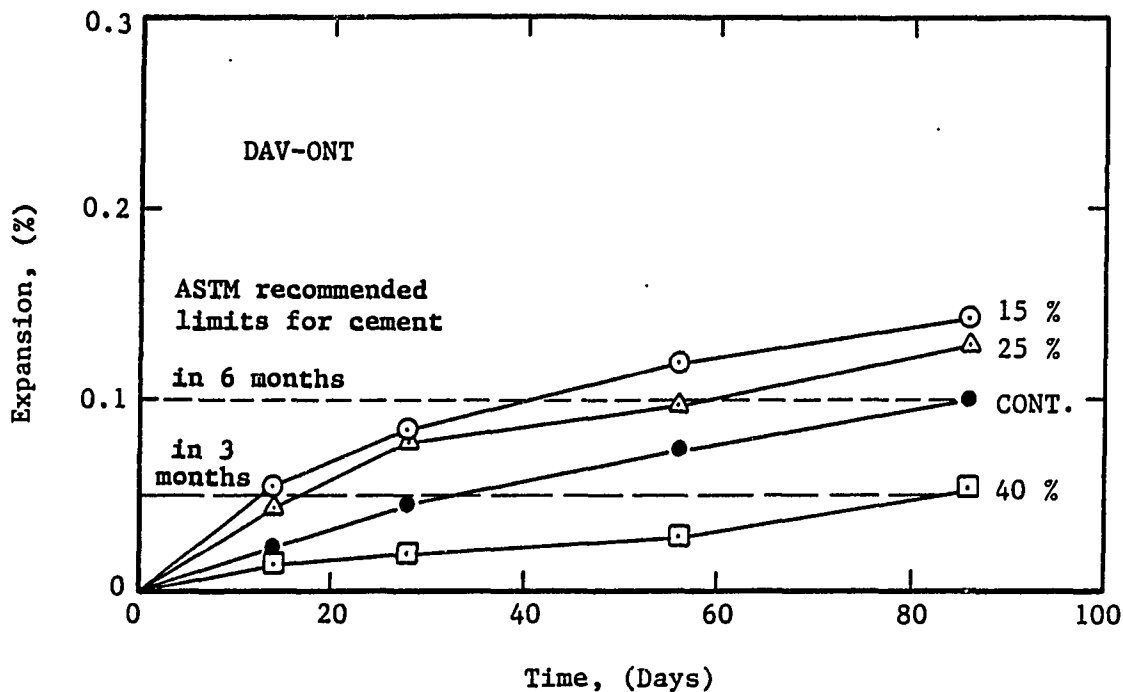
FIGURE 23. Effects of ONT fly ash on DAV cement expansion

FIGURE 24. Effects of OTT fly ash on DAV cement expansion
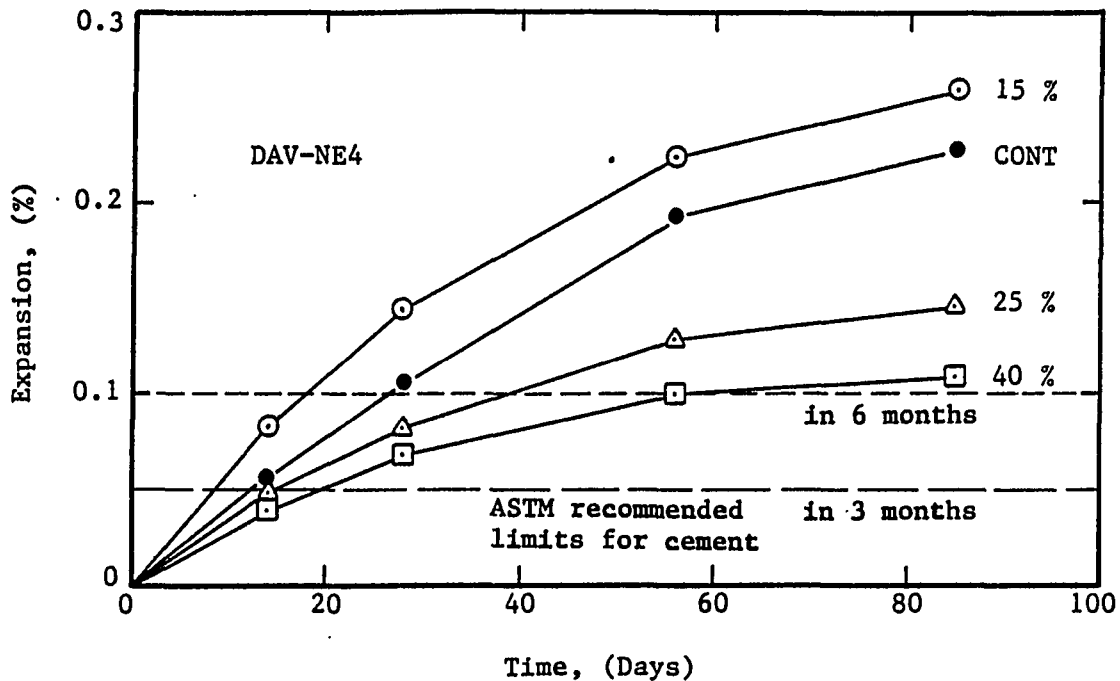
FIGURE 25. Effects of NE4 fly ash on DAV cement expansion

Expansions for mortars containing ND (low-alkali) cement with 0, 15, 25 and 40 percent replacements of ONT, OTT and NE4 fly ashes are shown in Figures 26, 27 and 28, respectively. Mortar containing ND cement without fly ash exhibited negligible amount of expansion or a certain amount of negative expansion resulted from drying shrinkage. Thus, the requirement (ASTM C 150) that the use of low-alkali cement in the concrete containing reactive aggregate is essential to protect the concrete from alkali-aggregate reaction was reconfirmed in this study. However, replacements of ND cement with Class C fly ashes studied produced greater amount of expansions than the control mortars at all replacement levels.

The highest amount of expansion occurred at about 25 percent replacement which is considered to be the pessimum content of. fly ash for ND cement.
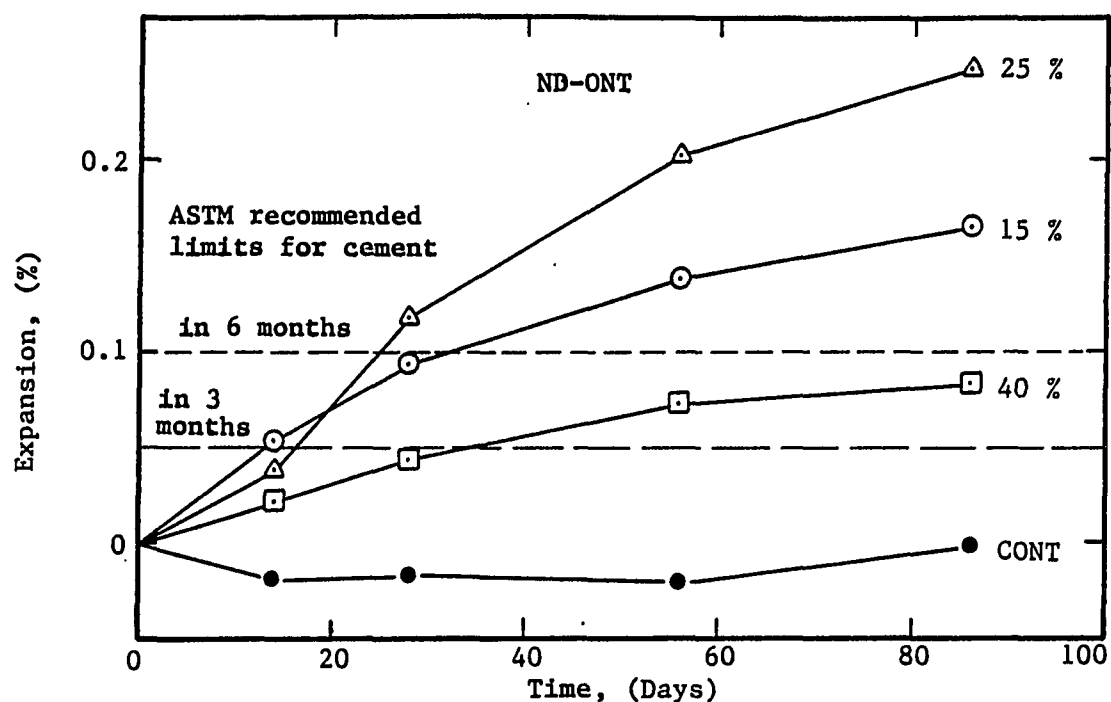
FIGURE 26. Effects of ONT fly ash on ND cement expansion

Figure 29 compares the effects of three Class C fly ashes on expansions of mortars containing DAV or ND cement when cured at 38°C for 12 weeks. None of the fly ashes was found to be acceptable as a mineral admixture for use in combination with a high-alkali cement and an alkali reactive aggregate according to ASTM C 441 [2] which requires a minimum of 75% reduction in expansion of mortar with 25% replacement of fly ash as compared with the control mortar. This suggests that the use of fly ash
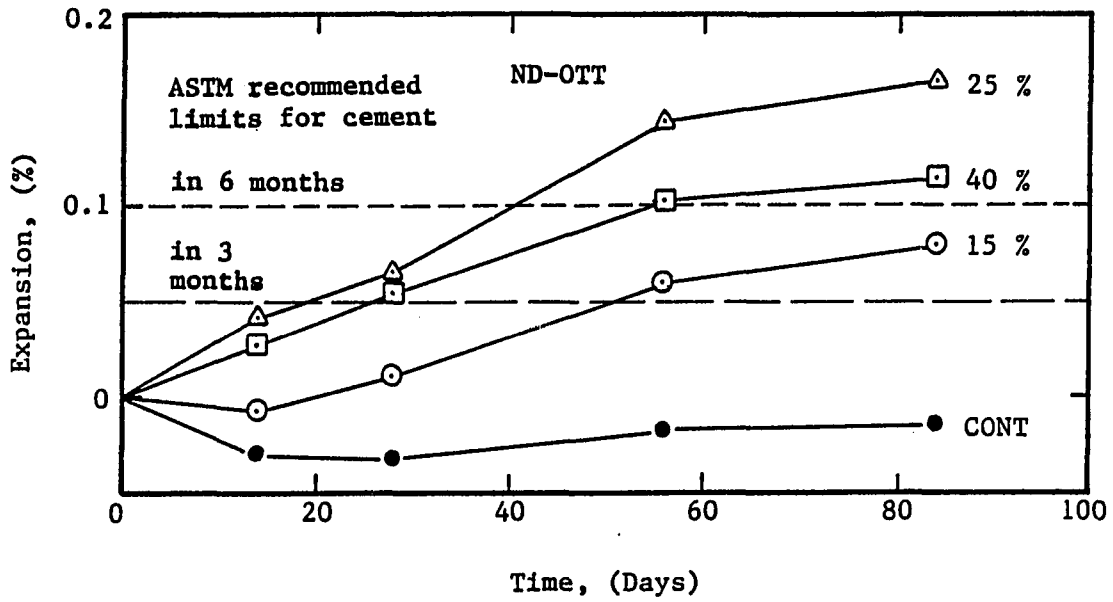
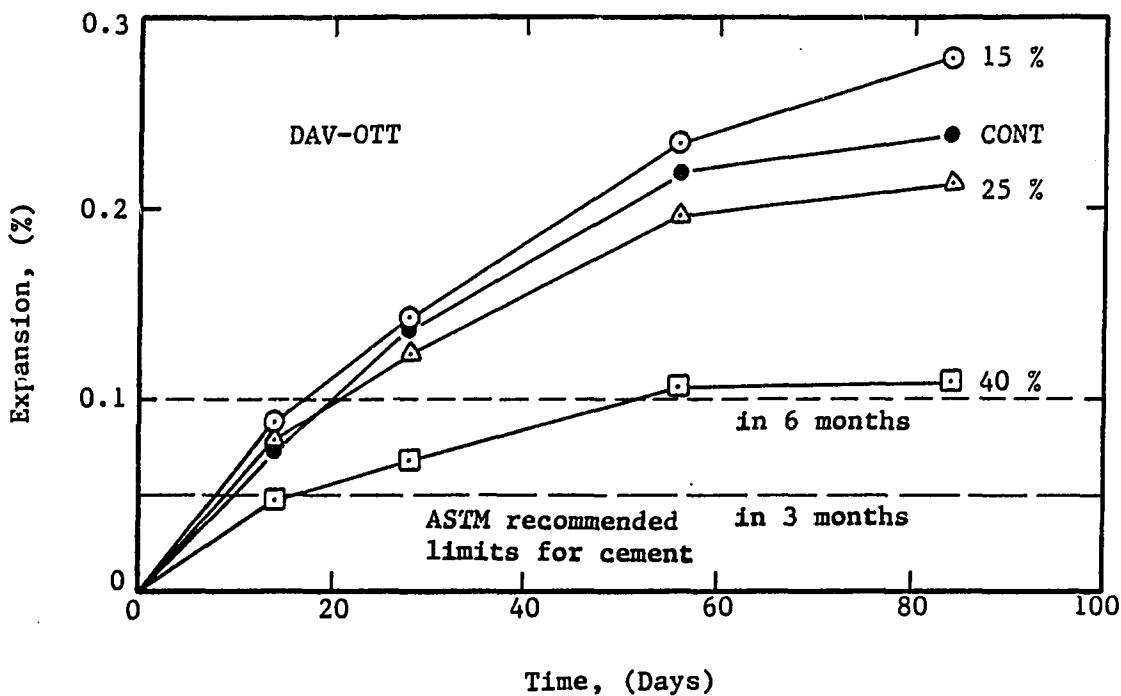FIGURE 27. Effects of OTT fly ash on ND cement expansion
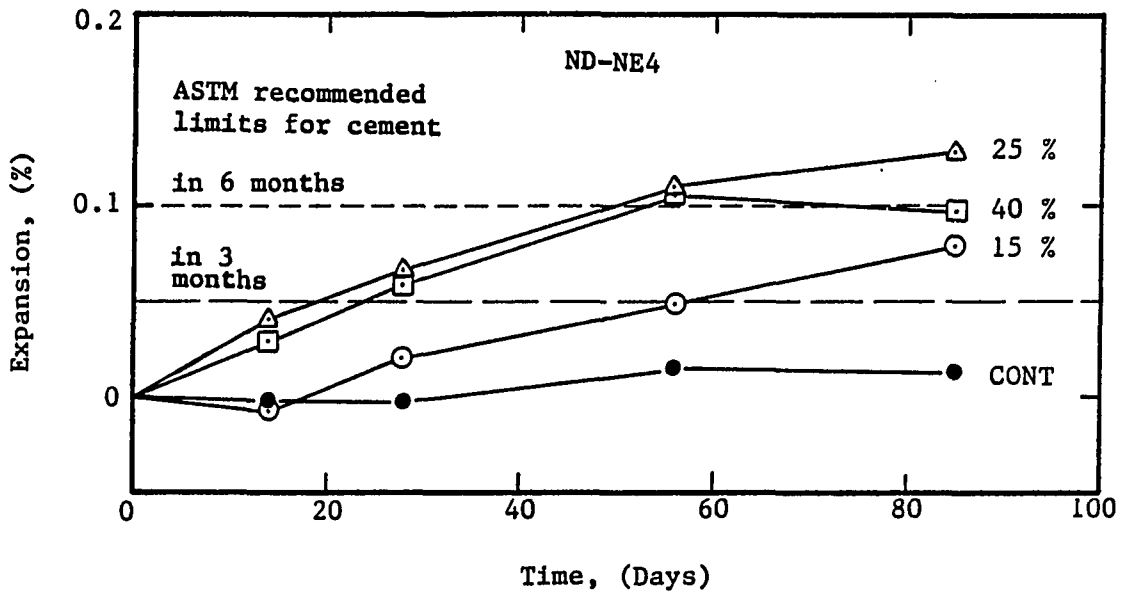
FIGURE 28. Effects of NE4 fly ash on ND cement expansion

as a mineral admixture to reduce the risk of alkali-aggregate reaction in concrete can not simply be based on the maximum limit of 1.5% eq. Na_2O (ASTM C 618) for available alkali content of fly ash, measured according to ASTM C 311. The available alkali content of NE4 fly ash is acceptable by ASTM C 618 specifications but not acceptable by ASTM C 441 mortar bar expansion test. It is also interesting to note that replacement of either high or low-alkali cement with certain amounts of Class C fly ashes studied produced greater amount of expansion instead of reducing it. For ND cement mortar bars, expansion increased with increasing total alkali content of fly ash when less than 25% of the cement was replaced by the fly ash. The pessimum content of fly ash for each cement mortars was found to be increased when the alkali content in the cement was decreased.

The concentration of active alkalis extracted from cement-fly ash pastes using the procedure described earlier after 28 and 96 days of curing at 38°C are shown in Figures 30 through 35. The concentration of active alkalis, expressed as % equivalent Na_2O, as well as the total equivalent alkalis increased proportionally with the percentage of fly ash replacement. The active alkali concentrations increased with time approaching the total alkali concentrations in most of the pastes after 96 days of curing at 38°C.
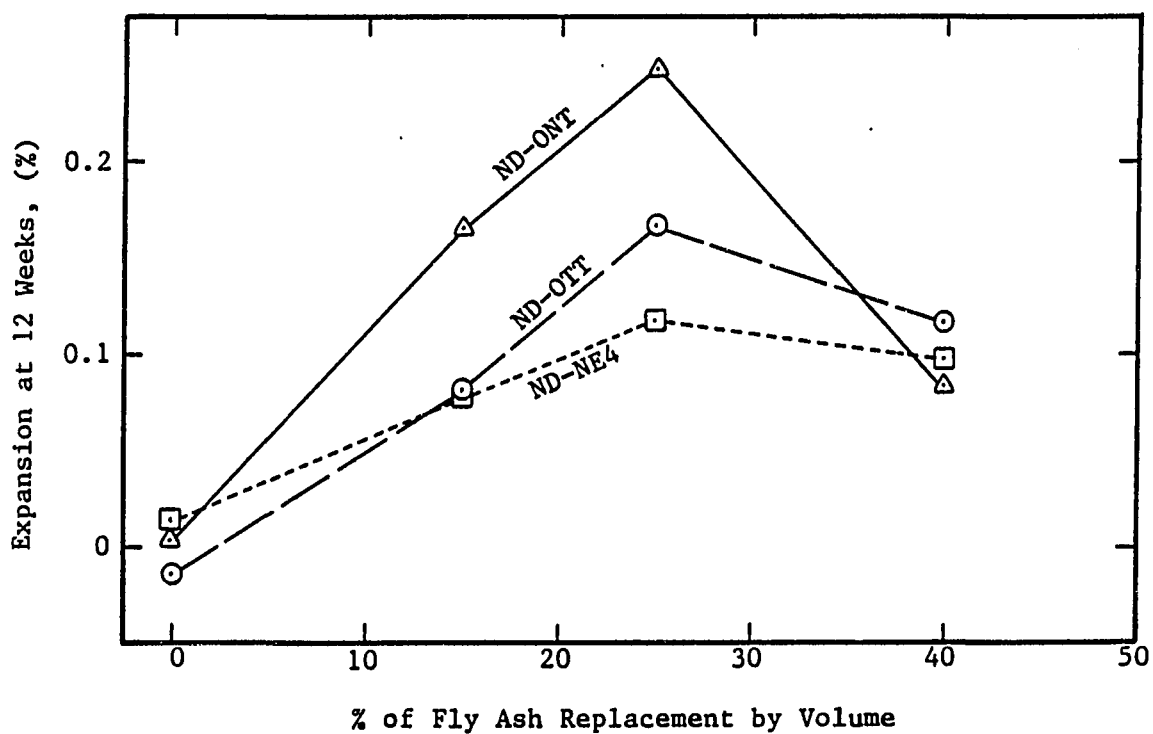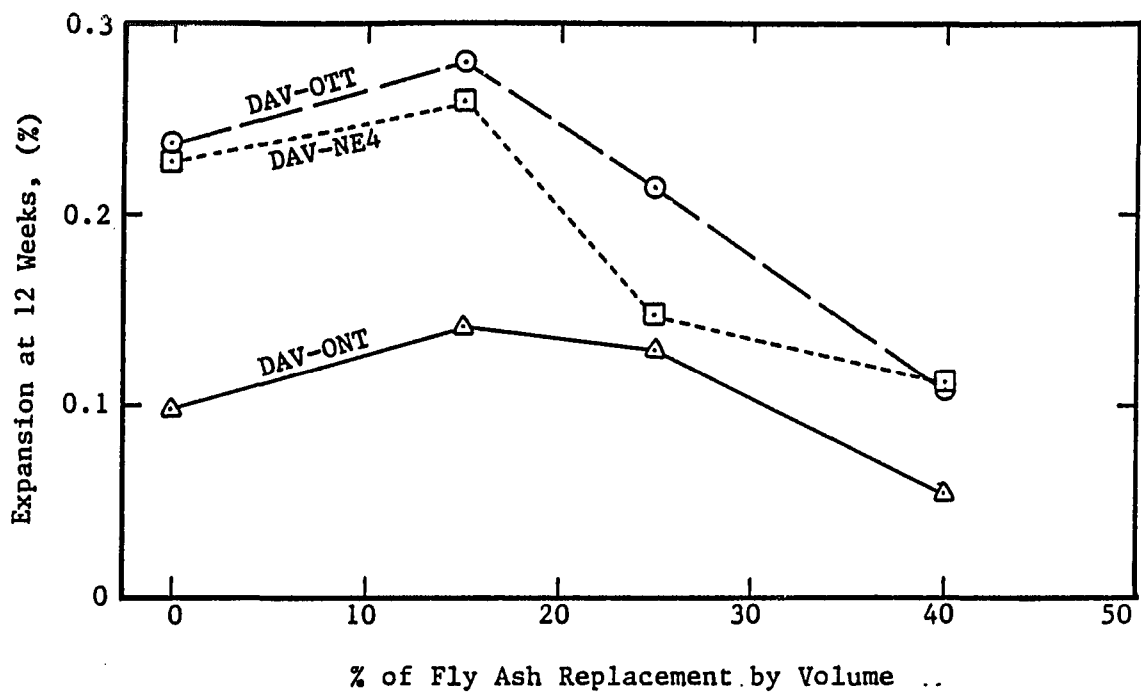
FIGURE 29. Comparison of ONT, OTT and NE4 fly ashes on DAV and ND cements expansion
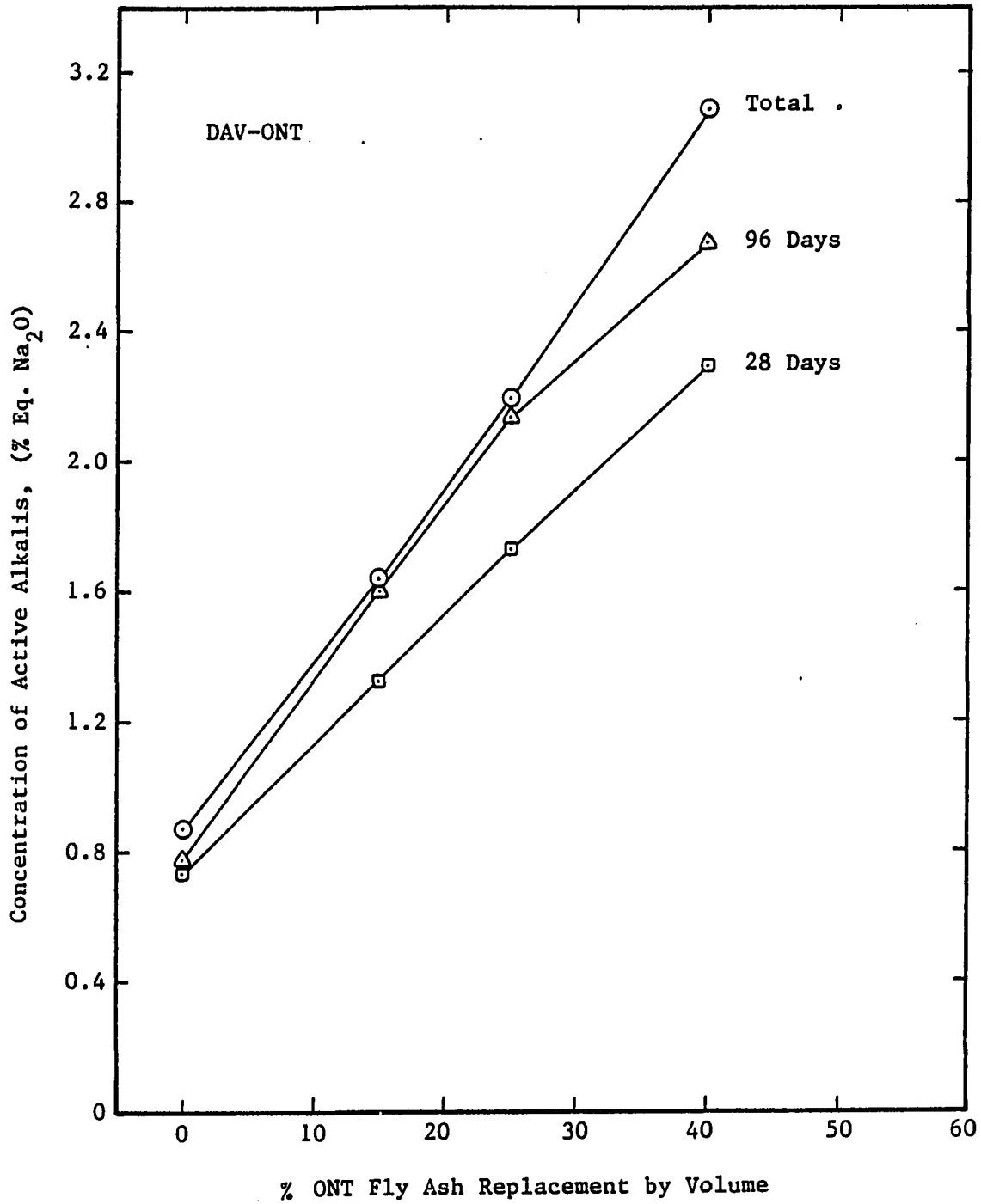
FIGURE 30. Concentration of active alkalis for DAV-ONT
paste
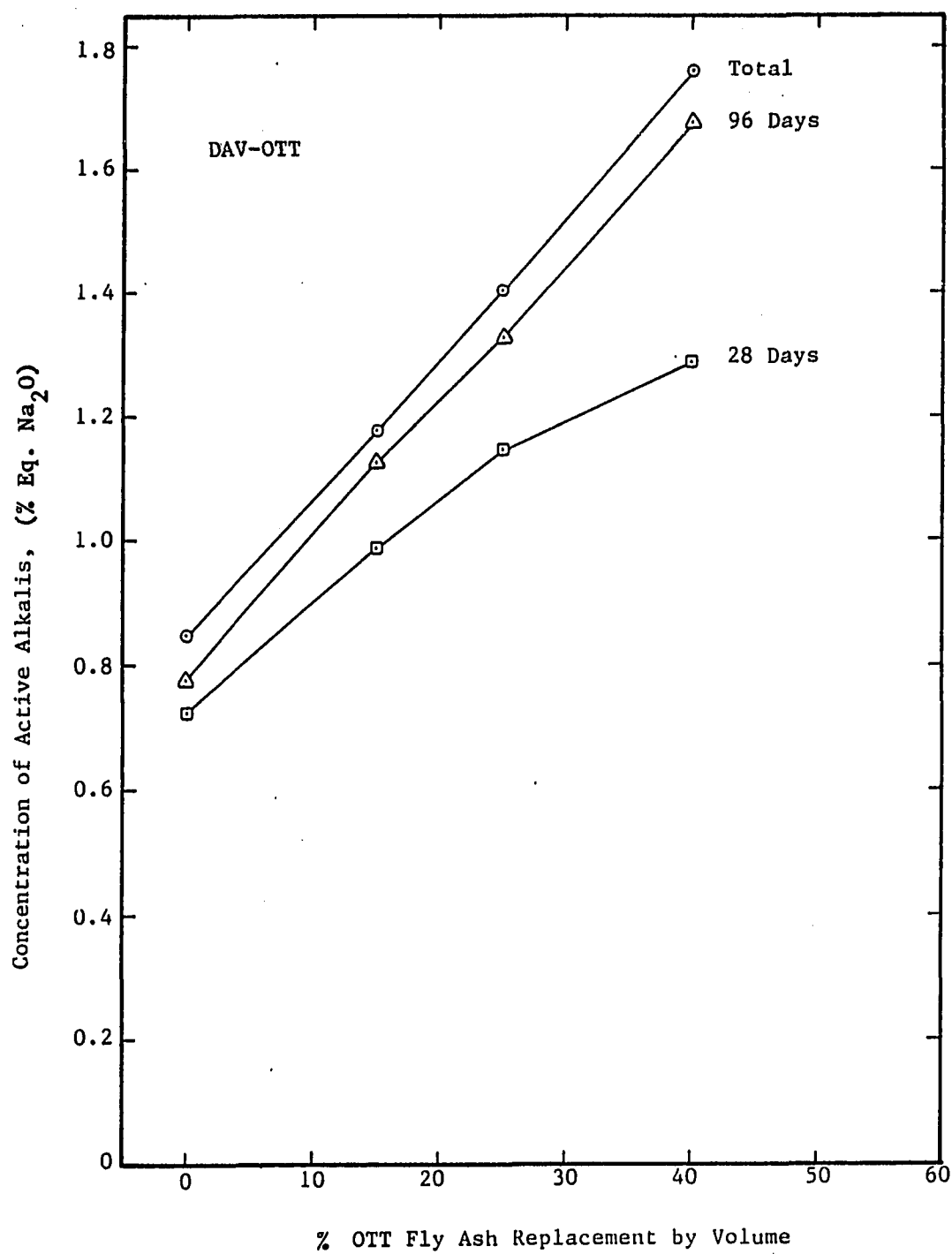
FIGURE 31. Concentration of active alkalis for DAV-OTT paste
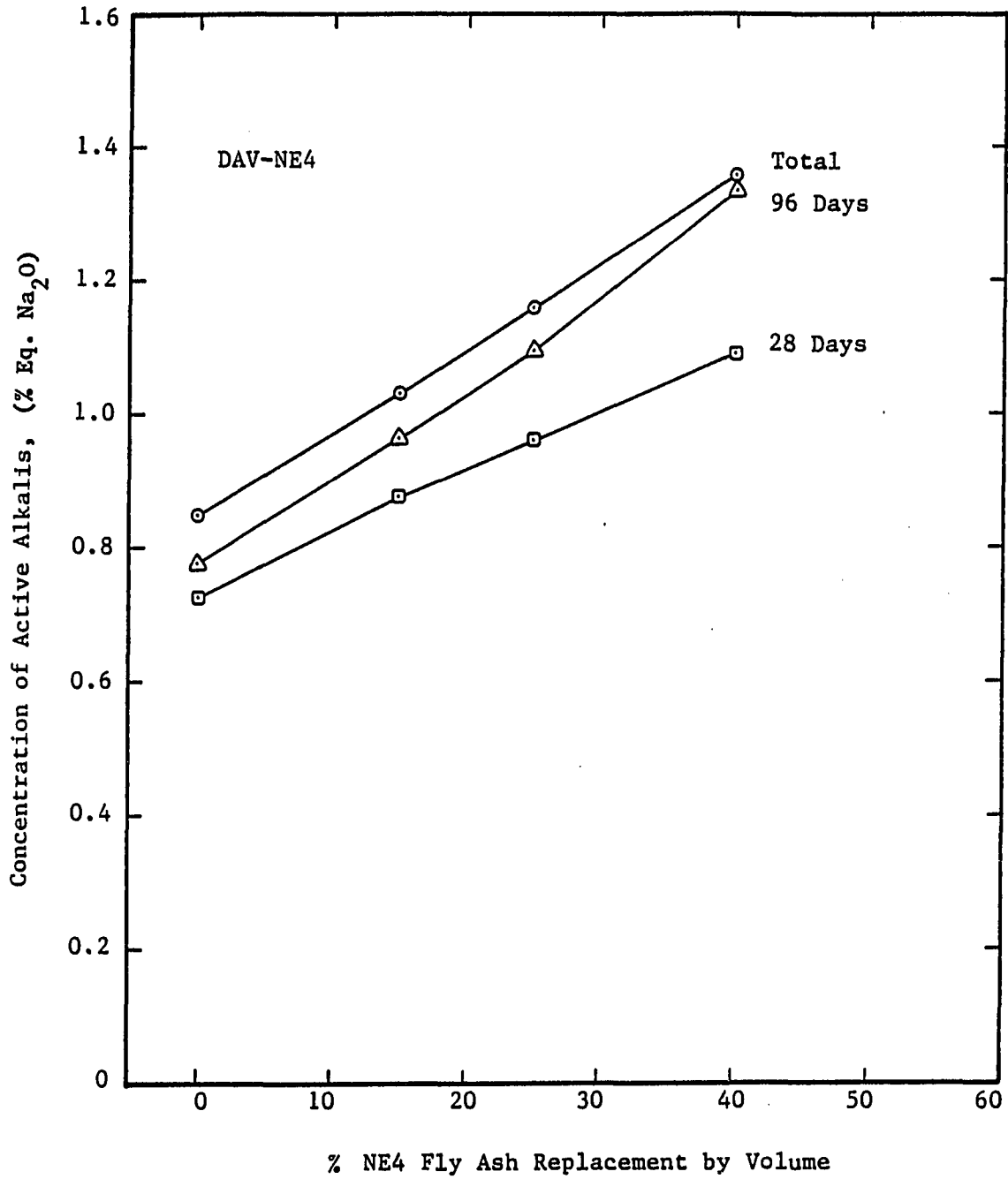
FIGURE 32. Concentration of active ·alkalis for DAV-NE4 paste
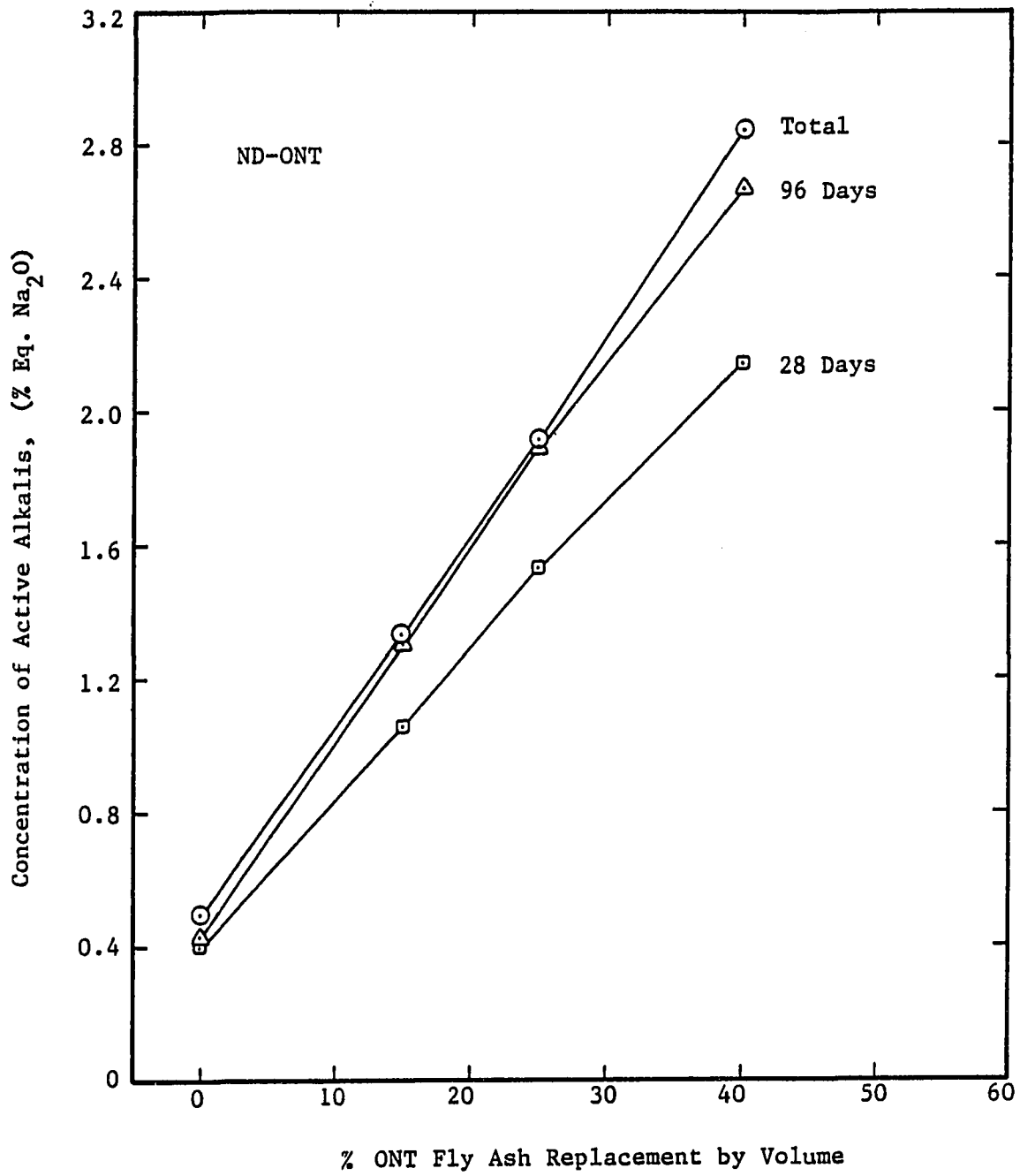
FIGURE 33. Concentration of active alkalis for ND-ONT paste
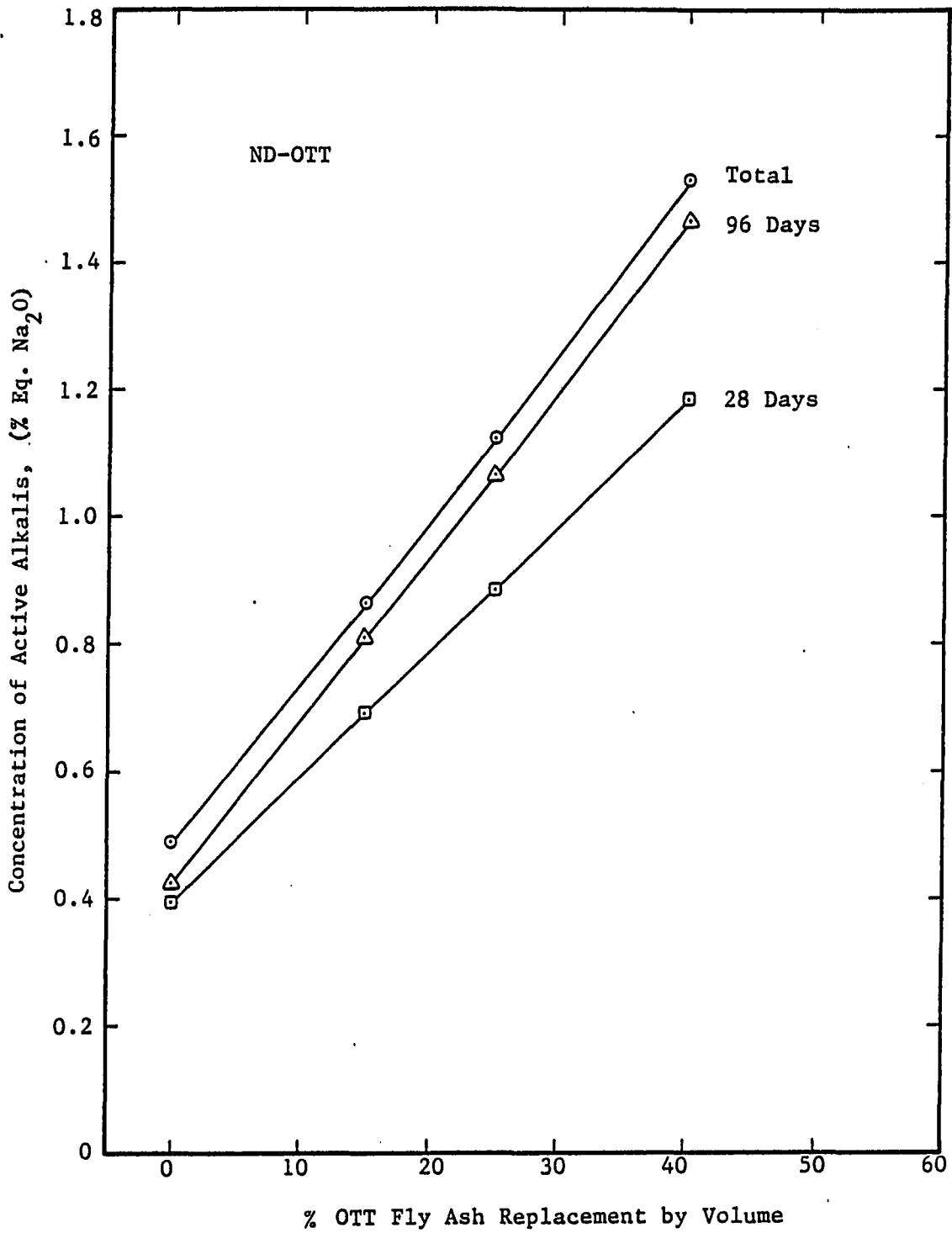
FIGURE 34. Concentration of active alkalis for ND-OTT paste
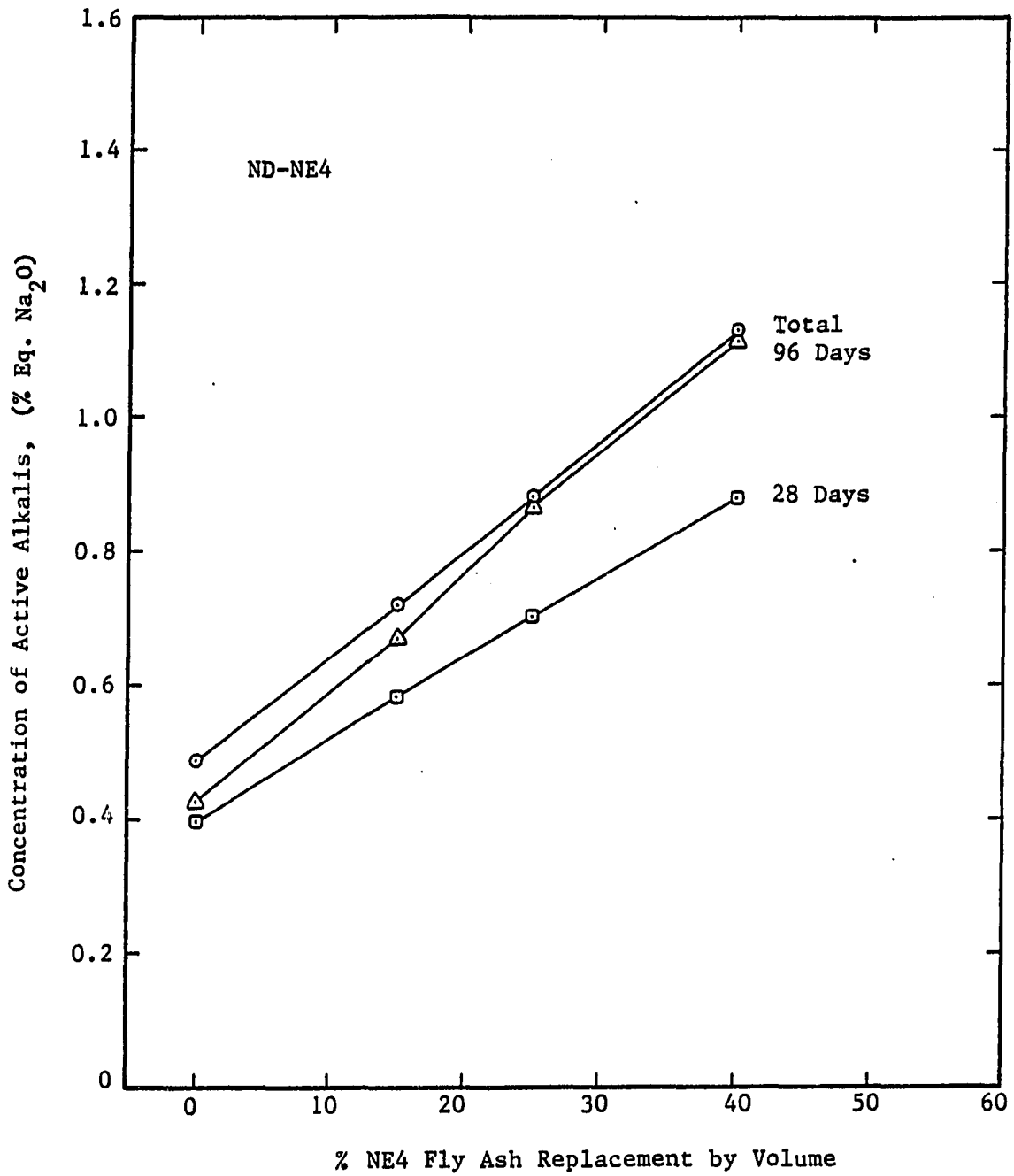
FIGURE 35. Concentration of active alkalis for ND-NE4 paste

The amount of active alkalis, expressed as the percentage of total equivalent alkalis, released from the cement-fly ash pastes are plotted in Figures 36, 37 and 38 as a function of fly ash replacement in mortar bars cured at 38°C for 28 and 96 days. When cured for 28 days, the amount of active alkalis steadily decreased with increasing percentage of fly ash replacement due to slow hydration of fly ash as compared with cement hydration. For all cement-fly ash pastes, more than 85% of total equivalent alkalis mobilized into the liquid phase becoming active for alkali-silica reaction after 96 days of curing. Greater amounts of sodium were extracted from all fly ash replaced pastes than from plain cement pastes at both curing periods. The difference in extracted potassium from plain and fly ash replaced pastes was not significant. Since the alkalis in all three fly ashes were predominantly sodium which was much greater than the sodium content in cement, the amount of active sodium extracted from fly ash replaced pastes was mobilized mainly from fly ash. Consequently, the concentration and the amount of active alkalis increased by replacement of a portion of Portland cement with Class C fly ash. In this study, about all of the alkalis contained in the cementitious materials of mortar tended to be active for alkali-silica reaction after long periods of curing. Thus, the total equivalent alkali content of fly ash replaced or plain cement pastes can be conservatively considered as active for

alkali-silica reaction.

Table 12 lists the calculated CaO/SiO_2 (C/S) and total equivalent Na_2O/SiO_2 (N/S) mole ratios of cement-fly ash pastes used in the mortar bar tests, and the concentrations of active alkalis measured after 96 days of curing at 38°C. Figure 39 shows that good linear relationship exists between the concentration of measured ultimate active alkalis, expressed as % equivalent Na_2O, and the N/S mole ratio in the paste. This indicates that the concentration of active alkalis in the pore solution depended not only on the total alkali content but also on the silica content of the paste. The concentration of active alkalis in the pore solution increases linearly with increasing N/S mole ratio in the paste which supports the observations discussed in previous sections. Data obtained from this phase of the study and data obtained earlier from the available alkali tests for six Iowa fly ashes are combined to get the regression equation shown in Figure 39. This regression equation can be used to estimate the concentration of active alkalis in cement-fly ash or fly ash-calcium hydroxide paste when the elemental composition in the reacting system is known.

Previously, it was suggested that the amount of available alkalis, expressed as the percentage of total equivalent alkalis, was dependent on the C/S mole ratio in the reacting system, and more than 85% of total equivalent alkalis might be
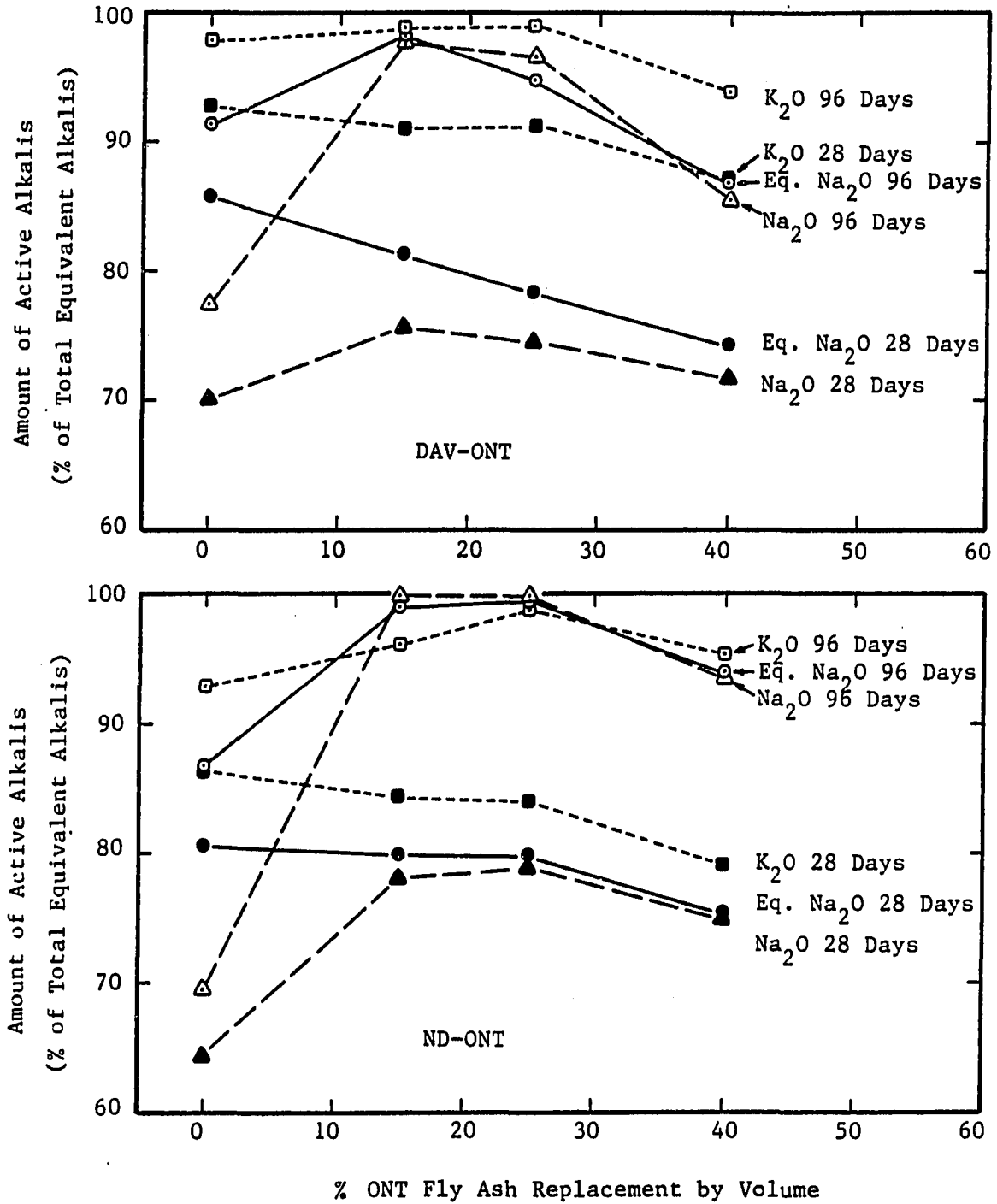
FIGURE 36. Amount of active alkalis extracted from DAV-ONT and ND-ONT pastes
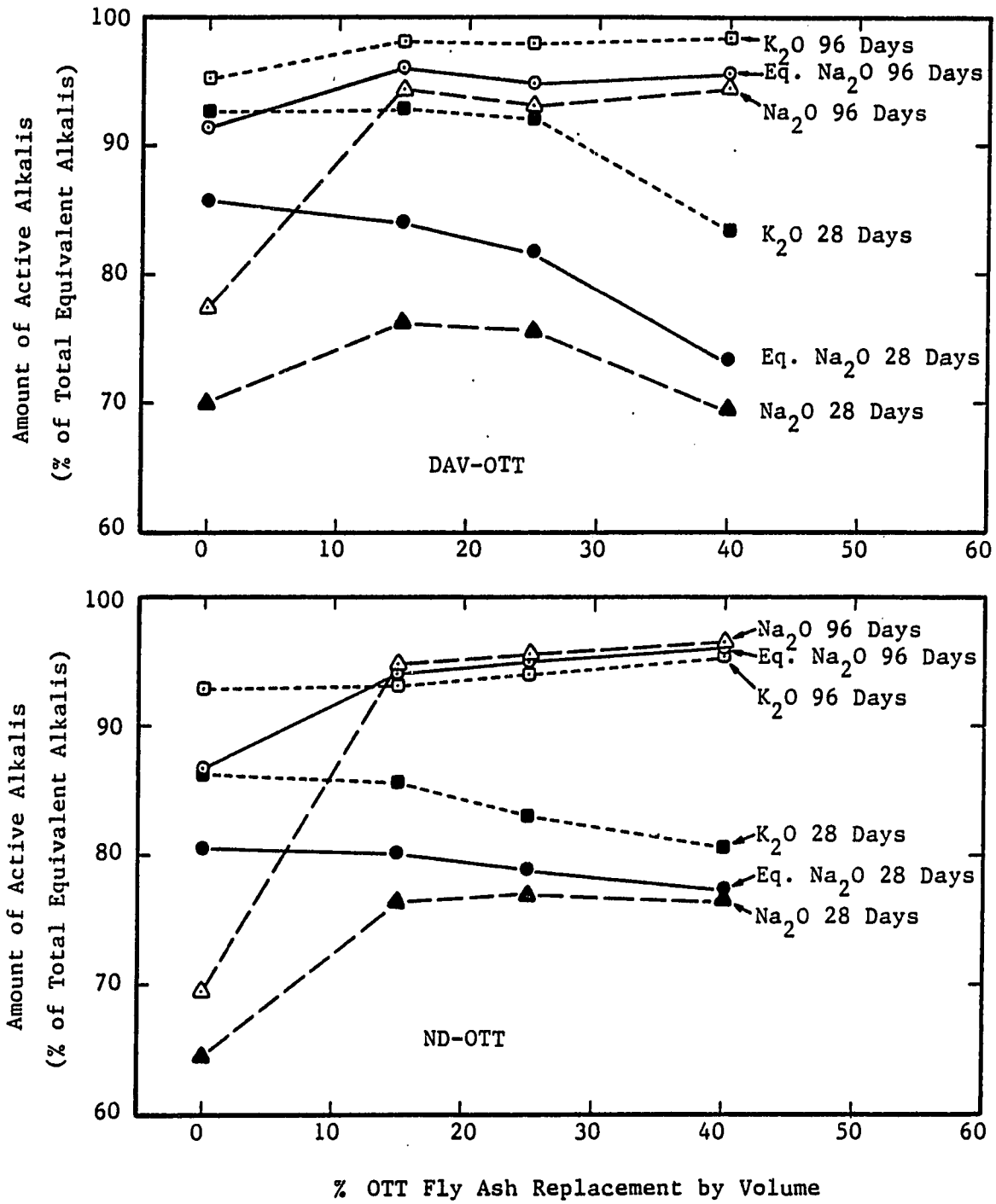
FIGURE 37. Amount of active alkalis extracted from DAV-OTT and ND-OTT pastes
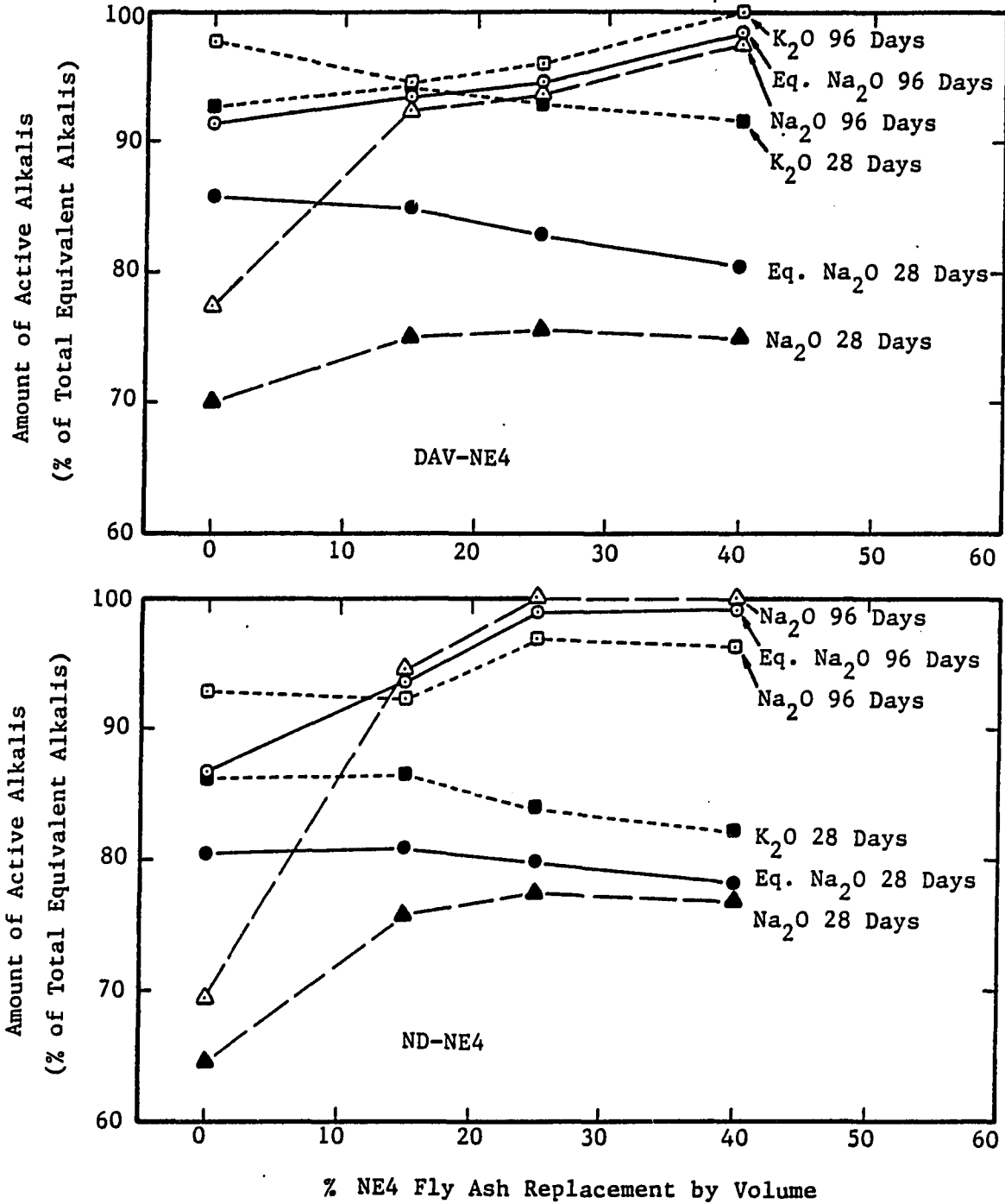
FIGURE 38. Amount of active alkalis extracted from DAV-NE4
and ND-NE4 pastes

TABLE 12.   Mole ratios of oxides and active alkali contents
for cement-fly ash pastes corresponding to the
paste used in mortar bar tests

| | Mole Ratio | | Active Alkalis @ 12 Weeks | |
	CaO/SiO$_2$	Na$_2$O/SiO$_2$	% Eq. Na$_2$O	% of Total Eq. Alkalis
DAV-CONTROL	3.1029	0.0375	0.7730	91.41
DAV-ONT-15%	2.5413	0.0655	1.6022	98.17
DAV-ONT-25%	2.2039	0.0824	2.1287	97.20
DAV-ONT-40%	1.7472	0.1052	2.6698	86.68
DAV-OTT-15%	2.7029	0.0492	1.1263	96.04
DAV-OTT-25%	2.4489	0.0566	1.3267	94.72
DAV-OTT-40%	2.0867	0.0672	1.6776	95.49
DAV-NE4-15%	2.6933	0.0427	0.6701	93.46
DAV-NE4-25%	2.4372	0.0459	0.8662	98.85
DAV-NE4-40%	2.0782	0.0505	1.1140	99.03
ND-CONTROL	3.1089	0.0213	0.4227	86.57
ND-ONT-15%	2.5529	0.0523	1.3027	98.77
ND-ONT-25%	2.2170	0.0710	1.8980	99.53
ND-ONT-40%	1.7607	0.0964	2.6661	93.87
ND-OTT-15%	2.7129	0.0356	0.8095	93.99
ND-OTT-25%	2.4602	0.0448	1.0653	95.02
ND-OTT-40%	2.0985	0.0584	1.4677	96.10
ND-NE4-15%	2.7131	0.0294	0.9608	93.40
ND-NE4-25%	2.4485	0.0345	1.0920	94.49
ND-NE4-40%	2.0898	0.0417	1.3309	98.28

ultimately mobilized to the liquid phase when the C/S mole
ratio was greater than 1.75. The C/S and N/S mole ratios and
active alkali contents (after 12 weeks of curing) of the
cement-fly ash pastes are listed in Table 12. The C/S mole

% Eq. $Na_2O = -0.1486 + 28.6153$ (N/S)

R = 0.9515

□ Available Alkali Test

⊙ Mortar Bar Test

Active Alkali Content, (% Eq. Na_2O)

Eq. Na_2O/SiO_2 Mole Ratio
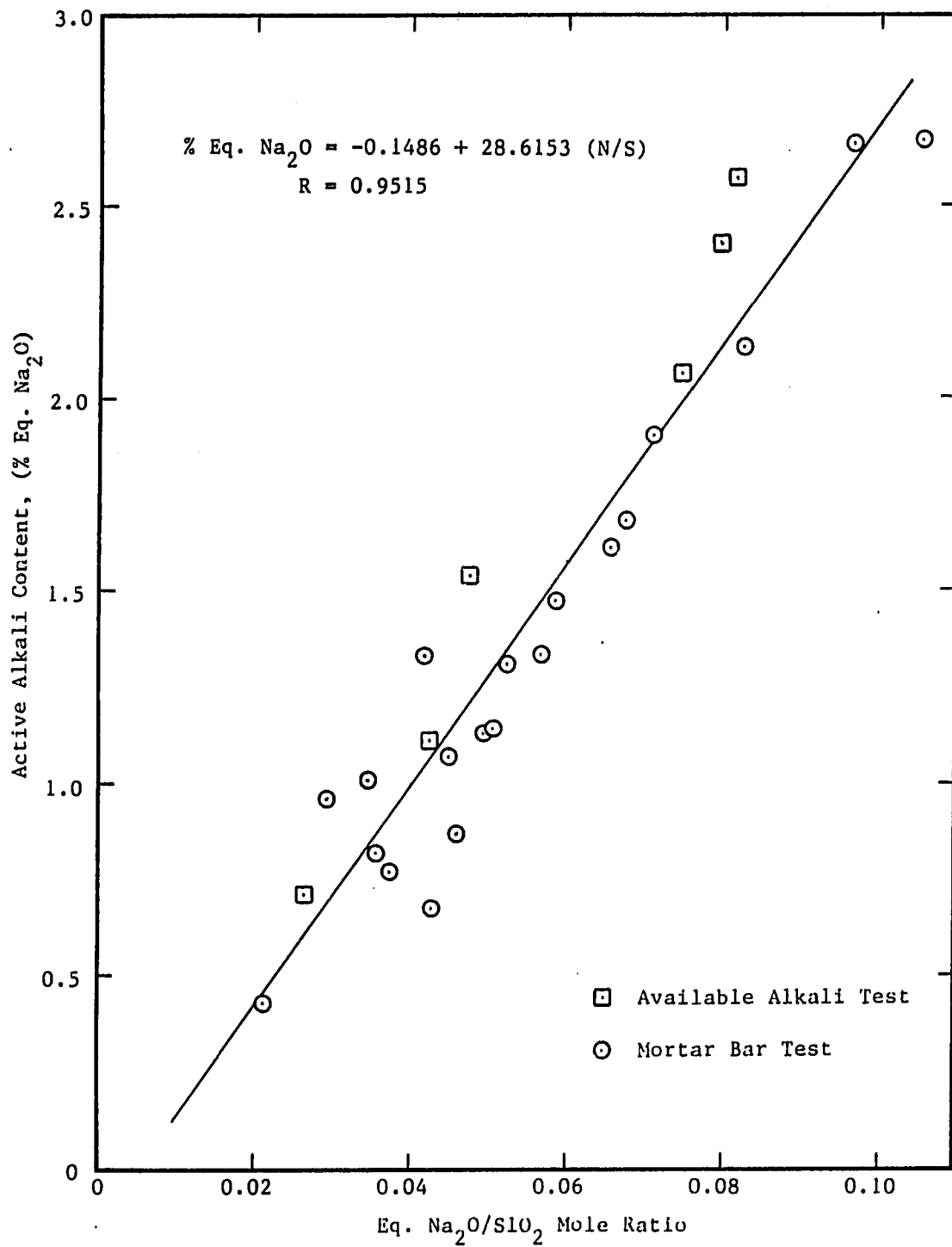
FIGURE 39. Relationship between concentration of ultimate active alkalis and N/S mole ratio

ratios ranged from 1.75 to 3.11, and the amount of ultimate

active alkalis for all of the cement-fly ash pastes were found

to be more than 85% of total equivalent alkalis supporting the

conclusions made in previous sections. This indicates that the

silica contents of fly ashes used in this study were not high

enough to reduce the C/S mole ratios of cement-fly ash pastes

effectively to the ideal range for retaining the alkalis in the

hydration products. In conclusion, the effectiveness of using

fly ash as a mineral admixture in concrete to reduce the risk

of deleterious alkali-silica reaction is dependent mainly on

the total alkali and silica contents in the fly ash. Fly ash

with higher silica and lower alkali contents would have better

effects on reducing damages caused by alkali-silica reaction.

Silica fume or Class F fly ash may be recommended as an

additional admixture for boosting SiO_2 content.

A hypothesis was made to explain the effects of alkalis in

fly ash on alkali-silica reaction. The results obtained from

this study showed increases in expansion for replacements of

high-alkali cement with small amounts of Class C fly ashes and

replacements of low-alkali cement with same fly ashes up to 40%

by volume. Figure 40 shows three curves. Each curve

represents the relationship between the measured 12-week

expansion, for replacements of both high and low-alkali cements

with each Class C fly ash (ONT, OTT and NE4), and the

corresponding N/S mole ratios of the cementitious materials in

mortar. The amount of expansion increased with increasing N/S mole ratio up to a certain level in each case. Beyond this level, expansion decreased with further increase in the N/S mole ratio. This indicates that a critical N/S mole ratio of the cementitious materials to produce maximum expansion may exist. The N/S mole ratio below or above this critical value would produce less expansion. As discussed in previous sections, the concentration of active alkalis in the pore solution tended to be proportional to the N/S mole ratio of the cementitious materials. According to Vivian [142], there was a pessimum (critical) alkali content to produce maximum expansion. When the amount of reactive component (opal or chert) in the aggregate was small, large addition of NaOH would reduce mortar bar expansion because the reaction products transformed rapidly from gel to liquid. His observation seemed also to be suitable for Pyrex glass as the reactive aggregate in mortars studied. Since each fly ash had different compositions and characteristics, each fly ash provided different effects on the critical N/S mole ratio. Fly ashes with higher alkali contents tended to have larger critical N/S mole ratios. However, more work is needed to confirm this hypothesis.

The results obtained from this study conflicted with the conclusion made by Dunstan [40]. He suggested that the minimum percentage of fly ash replacement to reduce alkali-aggregate
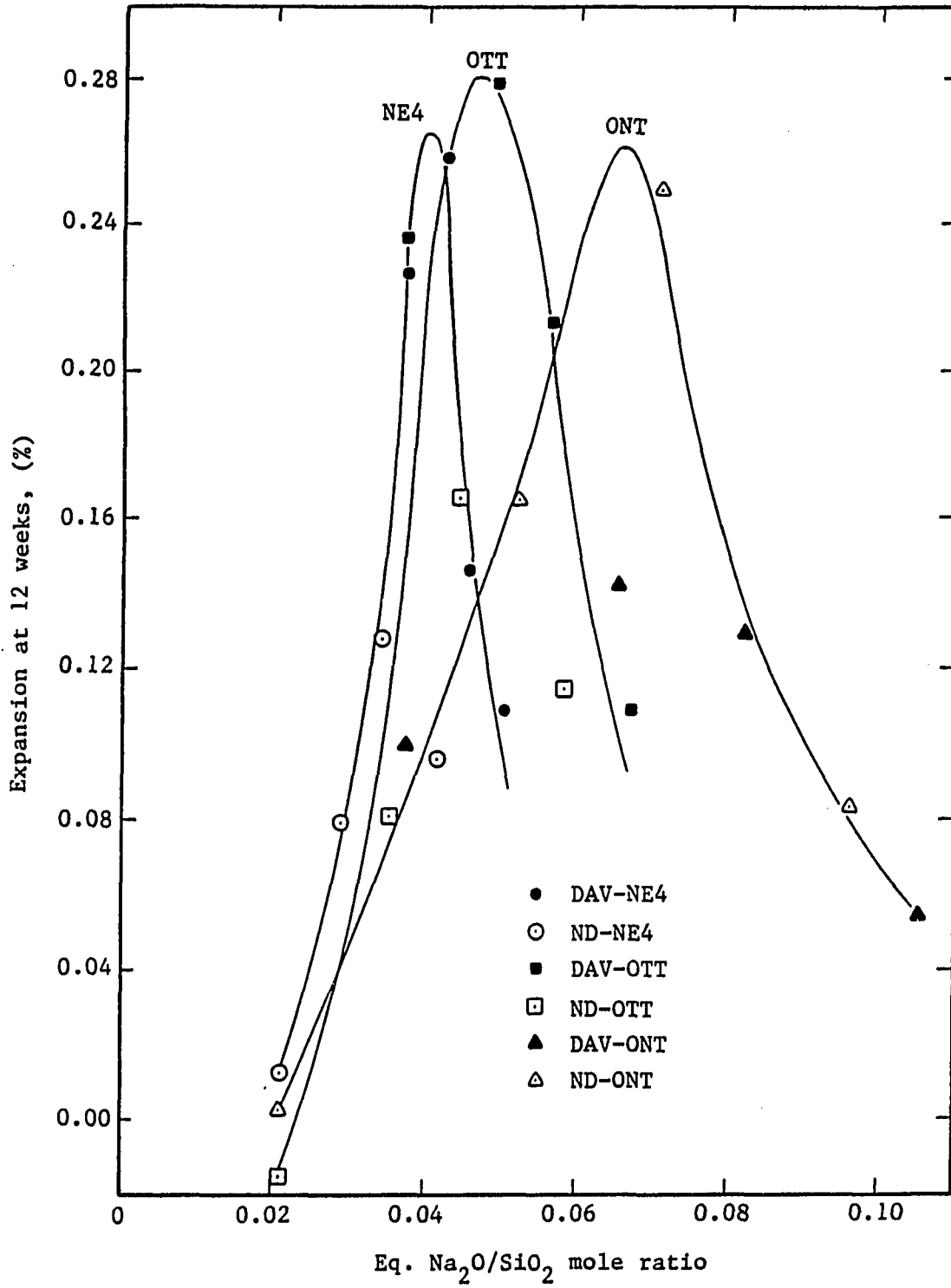
FIGURE 40. Effects of N/S mole ratio on mortar bar
expansions

reaction is approximately equal to the CaO percentage contained in the fly ash. Looking back to Table 9, the CaO contents of ONT, OTT and NE4 fly ashes were 13.10, 24.25 and 27.19, respectively. Expansions were not reduced by replacements of ND (low-alkali) cement with Class C fly ashes at percentages higher than their calcium contents. Replacements of DAV (high-alkali) cement with 15 and 25% ONT fly ash increased the expansions as compared with the control mortar.

Qualitative examination of reaction products was conducted using X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDXA). Figure 41 shows the X-ray diffractograms of hydrated mortar samples containing DAV cement and Pyrex glass with 1:1 weight ratio measured after 7 and 28 days of curing at 38°C. Figures 42 and 43 show the X-ray diffractograms of hydrated mortar samples with 25% of DAV cement replaced by ONT and NE4 fly ashes, respectively. The crystalline compounds in these hydrated mortars were mainly identified as calcium hydroxide, calcium carbonate and ettringite. Other crystalline hydration products detected could not be identified. Two weak and diffuse peaks around d-spacings of 4.07 and 3.04 angstorm were identified to be Pyrex glass and calcium silicate hydrates (C-S-H), respectively. The C-S-H is known to be an amorphous hydration product mainly derived from cement hydration. The area of the halo, the area under the diffused peak, is considered to be a

function of the concentration of the amorphous component in the sample. In those Figures, the halo area for Pyrex glass decreased with curing time, but the halo area for C-S-H increased with curing age. It is interesting to note in Figure 41 that the ratio of Pyrex glass halo areas corresponding to 7 and 28 days of curing was approximately equal to that of C-S-H halo for DAV cement mortar, the ratios were 1.32 and 1.31, respectively. However, the halo areas for fly ash replaced mortars were complicated because of the interference of the amorphous halo from fly ash. Figures 42 and 43 indicate that fly ash replaced mortars cured for 28 days had less calcium hydroxide content than the 7-day cured mortars in contrast with plain cement mortars. This may be attributed to the pozzolanic reaction between fly ash and calcium hydroxide produced from cement hydration. Chatterji [19] investigated several damaged concrete structures and reported that the presence of free calcium hydroxide is the necessary condition for the breakdown of a Portland cement concrete structure due to alkali-silica reaction. The consumption of calcium hydroxide in fly ash replaced mortars might be one of the reasons for the reduction in expansion caused by alkali-silica reaction. Because none of the raw materials used in these experiments was pure and the reaction products were so poorly crystallized, the reaction products obtained from such a complicate alkali-silica reaction could not be clearly identified by XRD analysis. If pure raw

materials are used and the crystallization of reaction products can be improved by raising curing temperatures, XRD method may give better defined peaks for identification of the reaction products from alkali-silica reaction.

Scanning electron microscopy (SEM) aided by energy dispersive X-ray analysis (EDXA) was also used for examining the reaction products. SEM samples were obtained from selected broken pieces of mortar bars. SEM pictures in Figures 44 through 47 show that the reaction products, known as alkali-silicate gel, had coated the Pyrex glass surfaces. The elemental analyses performed by EDXA indicated that the composition of alkali-silicate gel, which is composed mainly of silica, sodium, potassium, calcium and small amount of aluminum, varied along the surface. Figures 48 and 49 show that the alkali-silicate gel had penetrated into the cement matrix and voids.

A preliminary study to investigate the influence of alkalis from external sources, such as de-icing salts and sea water, on expansion of mortar bars with and without fly ash was conducted by immersing mortar bars in saturated NaCl solution as described earlier. Figures 50 and 51 show that the amount and the rate of mortar bar expansion were greatly increased and accelerated by immersing the mortar bars in saturated NaCl solution for both plain cement and fly ash replaced mortar bars. Expansion of mortar bars containing low-alkali cement
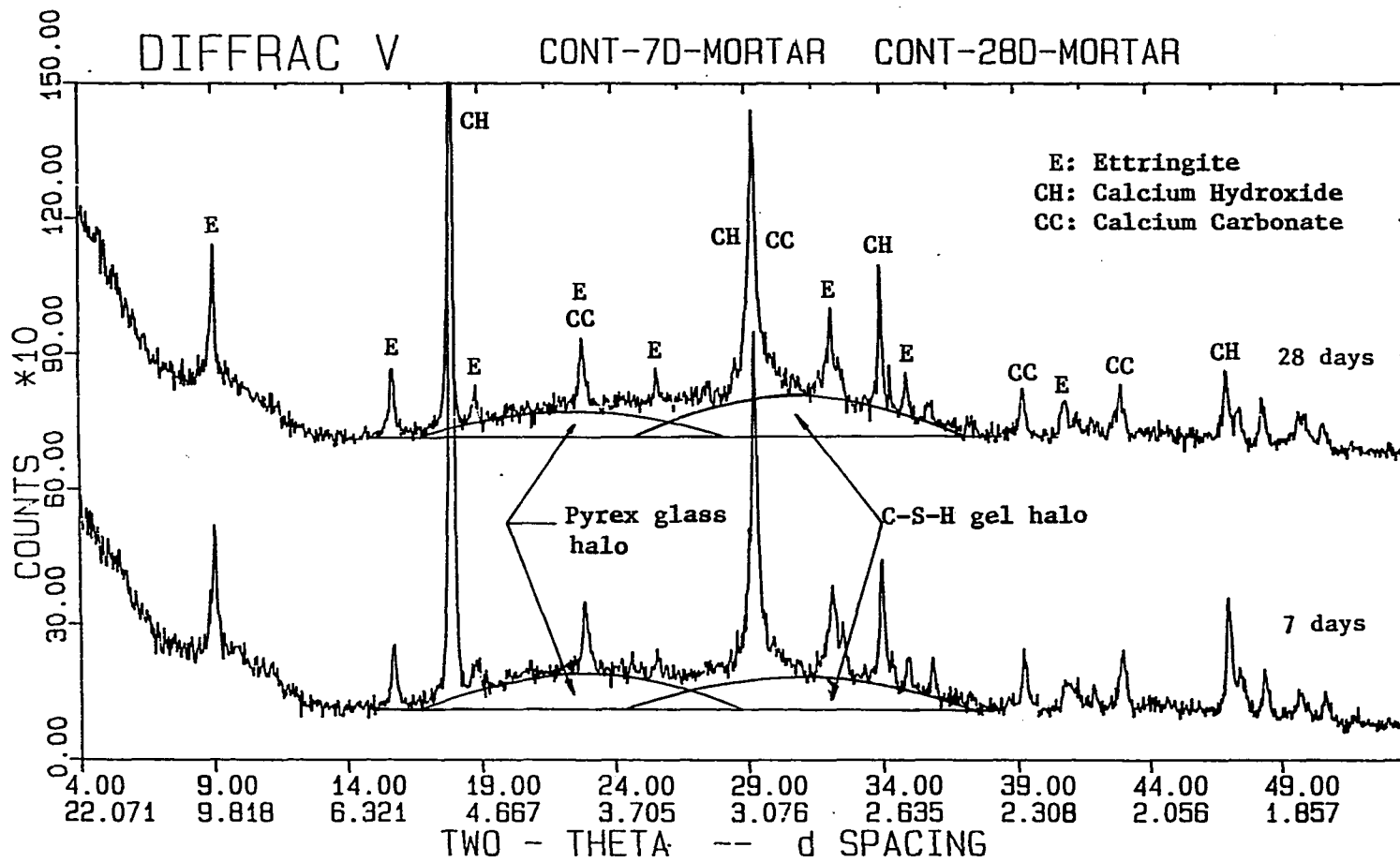
FIGURE 41. X-ray diffractograms, DAV cement and Pyrex glass with 1:1 mass ratio, cured at 38°C for 7 and 28 days
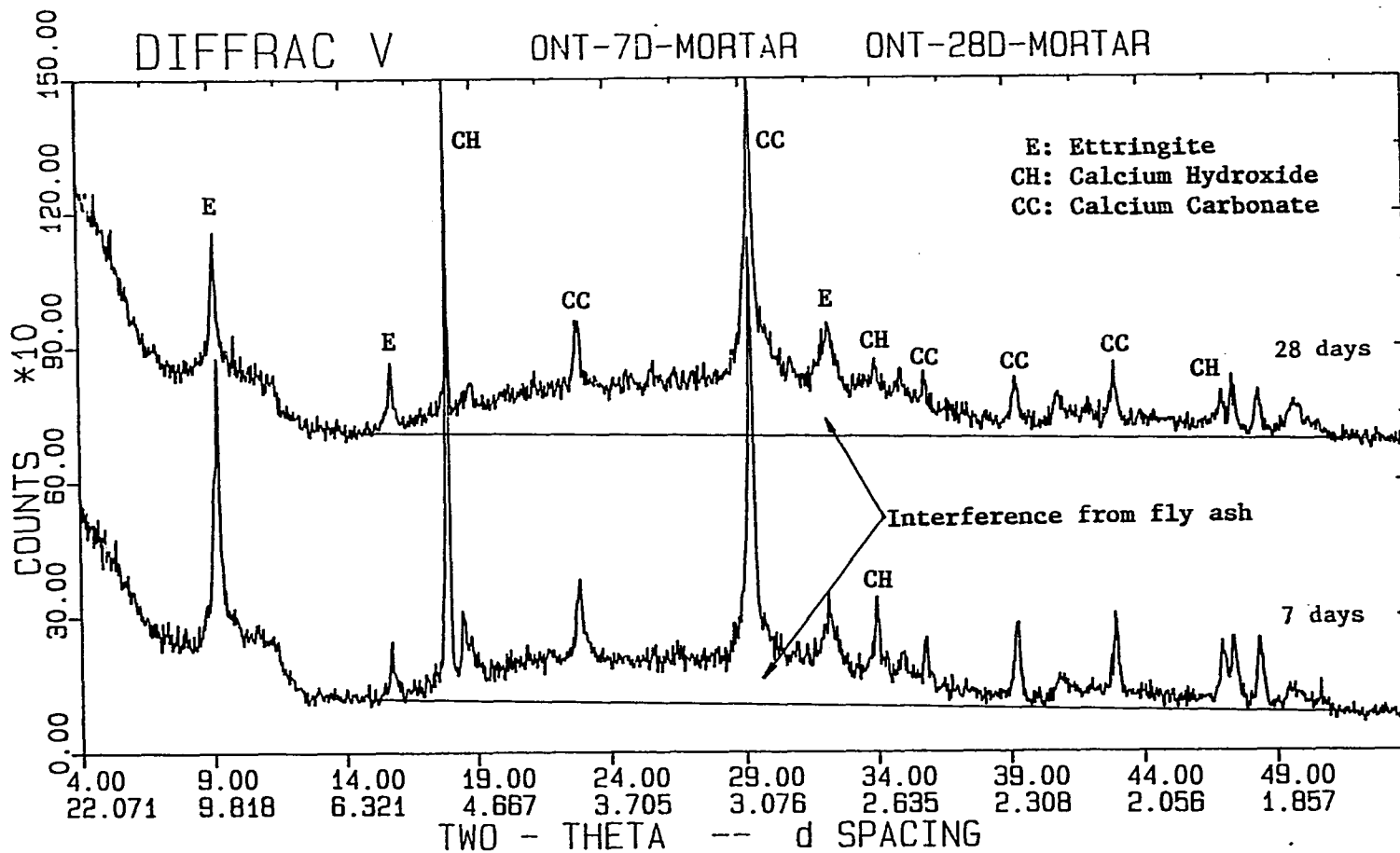
FIGURE 42. X-ray diffractograms, DAV cement with 25% replacement of ONT fly ash and Pyrex glass with 1:1 mass ratio, cured at 38°C for 7 and 28 days
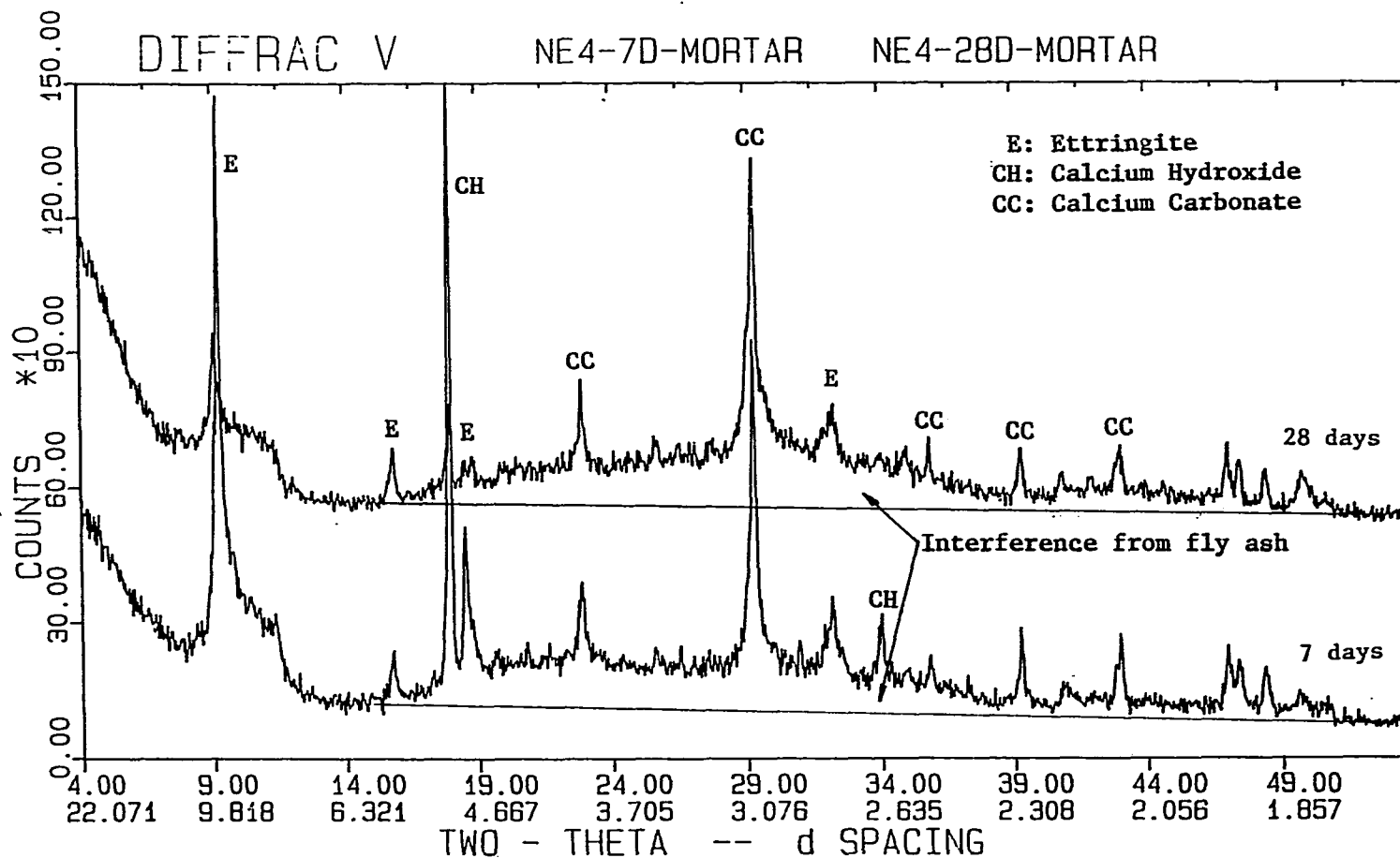
FIGURE 43. X-ray diffractograms, DAV cement with 25% replacement of NE4 fly ash and Pyrex glass with 1:1 mass ratio, cured at 38°C for 7 and 28 days
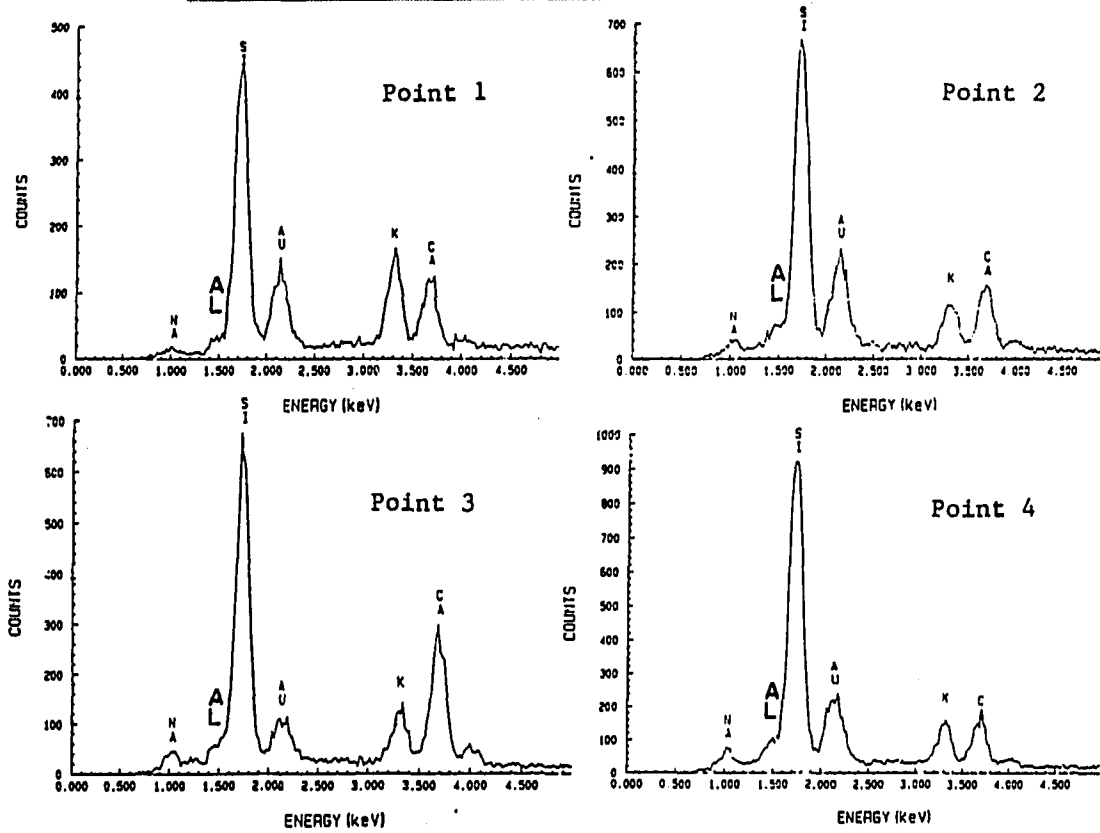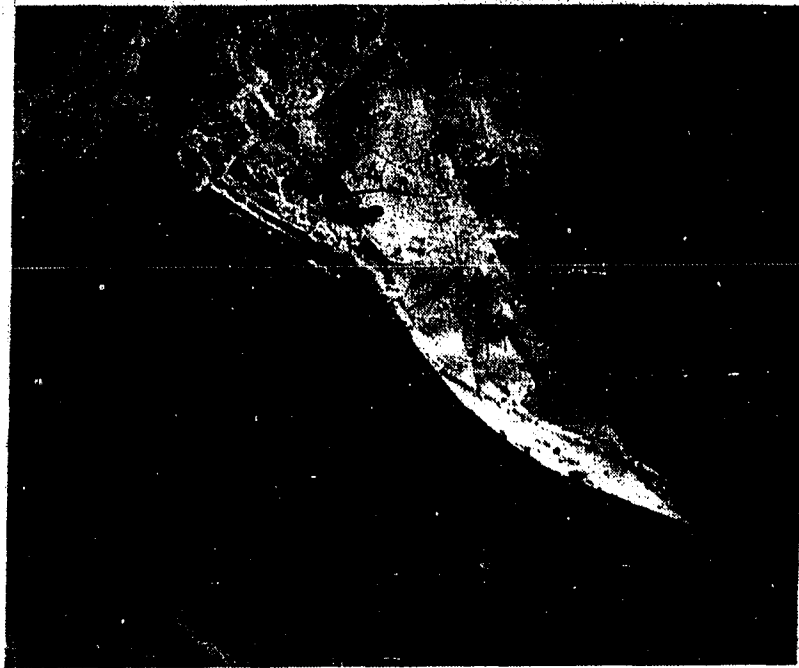
FIGURE 44. Scanning electron micrograph, DAV-ONT-15% mortar bar, cured at 38°C for 56 days, 80X
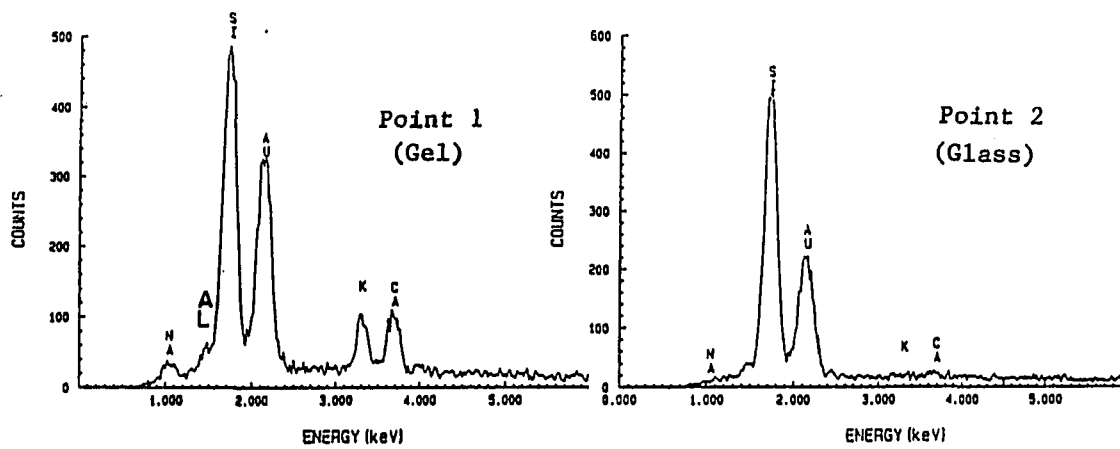
FIGURE 45.   Scanning electron micrograph, DAV-ONT-15% mortar
bar, cured at 38°C for 56 days, 80X
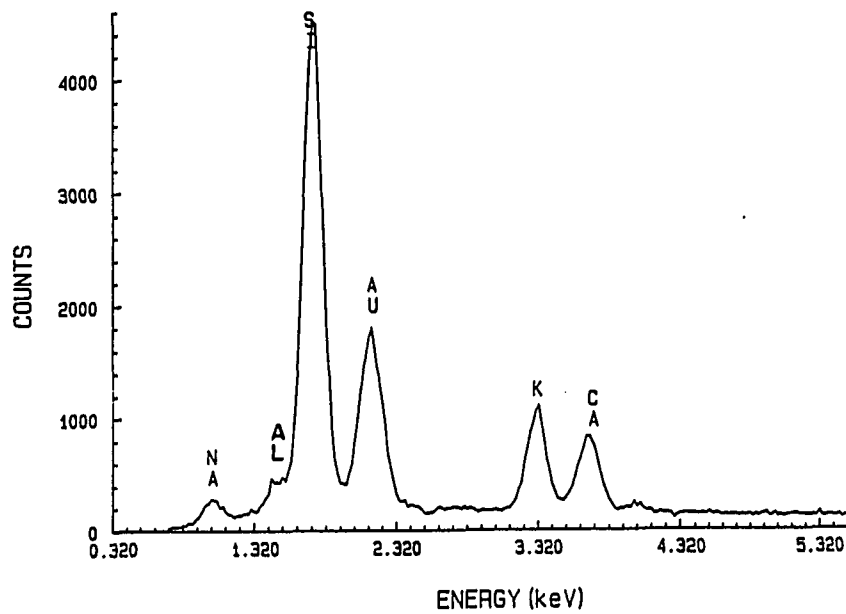
FIGURE 46. Scanning electron micrograph, DAV-ONT-25% mortar bar, cured at 38°C for 28 days, 150X
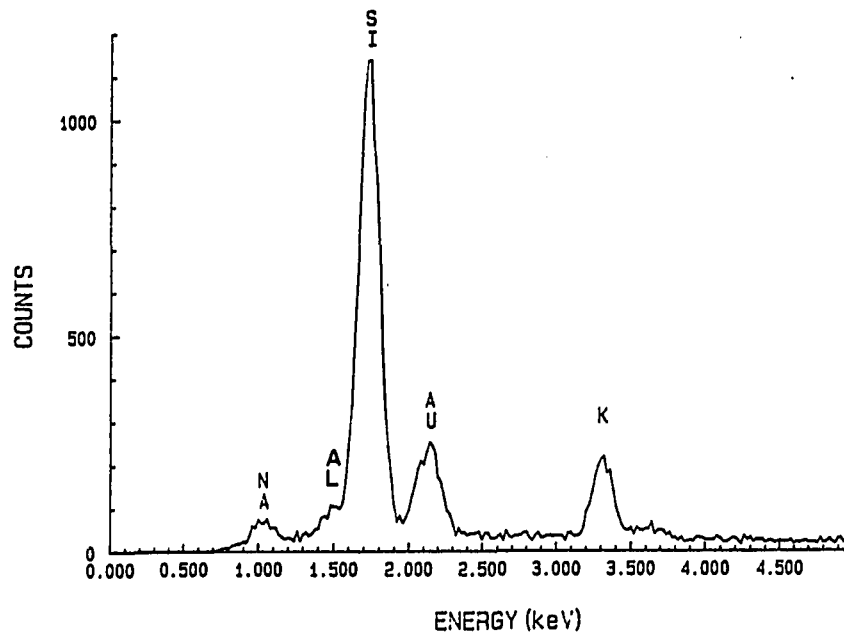
FIGURE 47.   Scanning electron micrograph, DAV-ONT-40% mortar
bar, cured at 38°C for 56 days, 200X
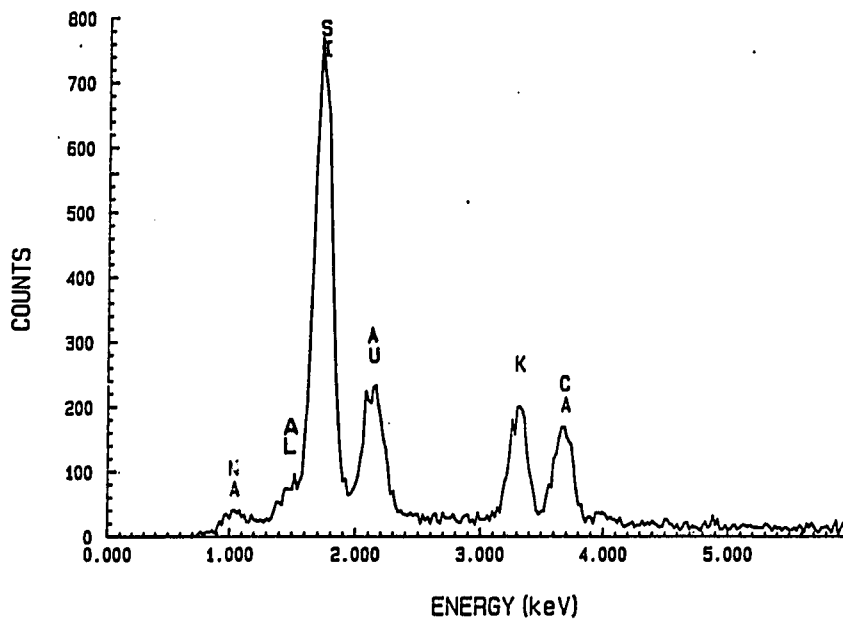
FIGURE 48. Scanning electron micrograph, DAV-CONTROL mortar
bar, cured at 38°C for 56 days, 120X
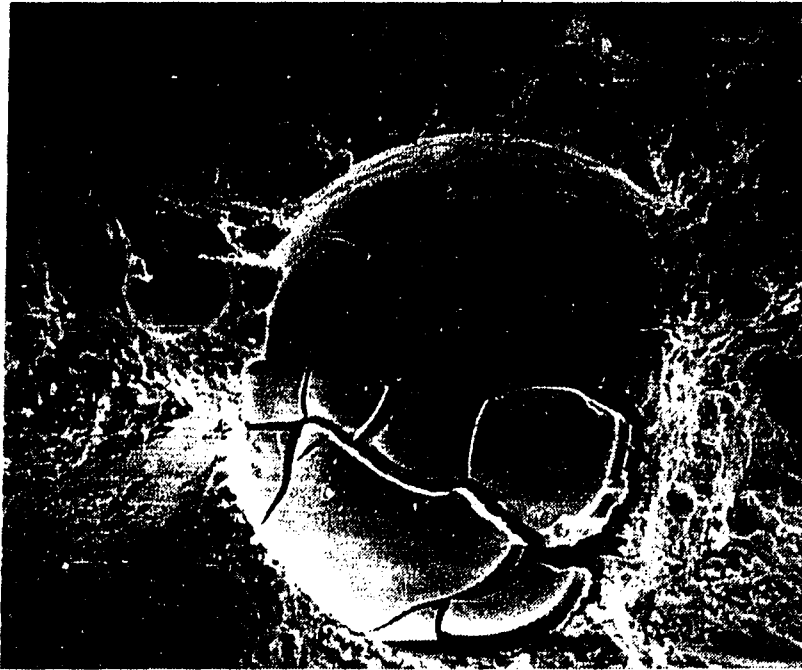
FIGURE 49. Scanning electron micrograph, DAV-ONT-40% mortar
bar, cured at 38°C for 56 days, 150X

without fly ash was greater than that containing high-alkali
cement without fly ash. However, expansions were reduced by
replacements of a portion of cement with fly ashes. The larger
the percentage of fly ash replacement, the greater the amount
of reduction in expansion.

Expansions measured at 12 weeks (56 days after immersing
in saturated NaCl solution) seemed inversely related to the N/S
mole ratio of the cementitious materials of the mortar, as
shown in Figure 52. A hypothesis is proposed to explain this
phenomenon. As discussed earlier, a mortar made with a paste
having a higher N/S mole ratio is expected to produce greater
concentration of active alkalis to react with Pyrex glass
faster than the martar made with lower N/S mole ratio paste.
A relatively small amount of silica is provided by a mortar
having a high N/S mole ratio to react and consume alkalis thus
leaving excess alkalis to react and form a thick alkali-
silicate gel coating on Pyrex glass. Thus, when mortar bars
were immersed in the saturated NaCl solution, a larger amount
of alkali-silicate gel has already formed around the glass
particles of mortar bars having high N/S mole ratios producing
a thick diffusion barrier for further diffusion of alkali ions
and water form external sources to attack glass particles.
Penetration of reaction products already formed into cement
matrix or voids might reduce the permeability of mortar to
delay further attack of alkalis from external sources. The
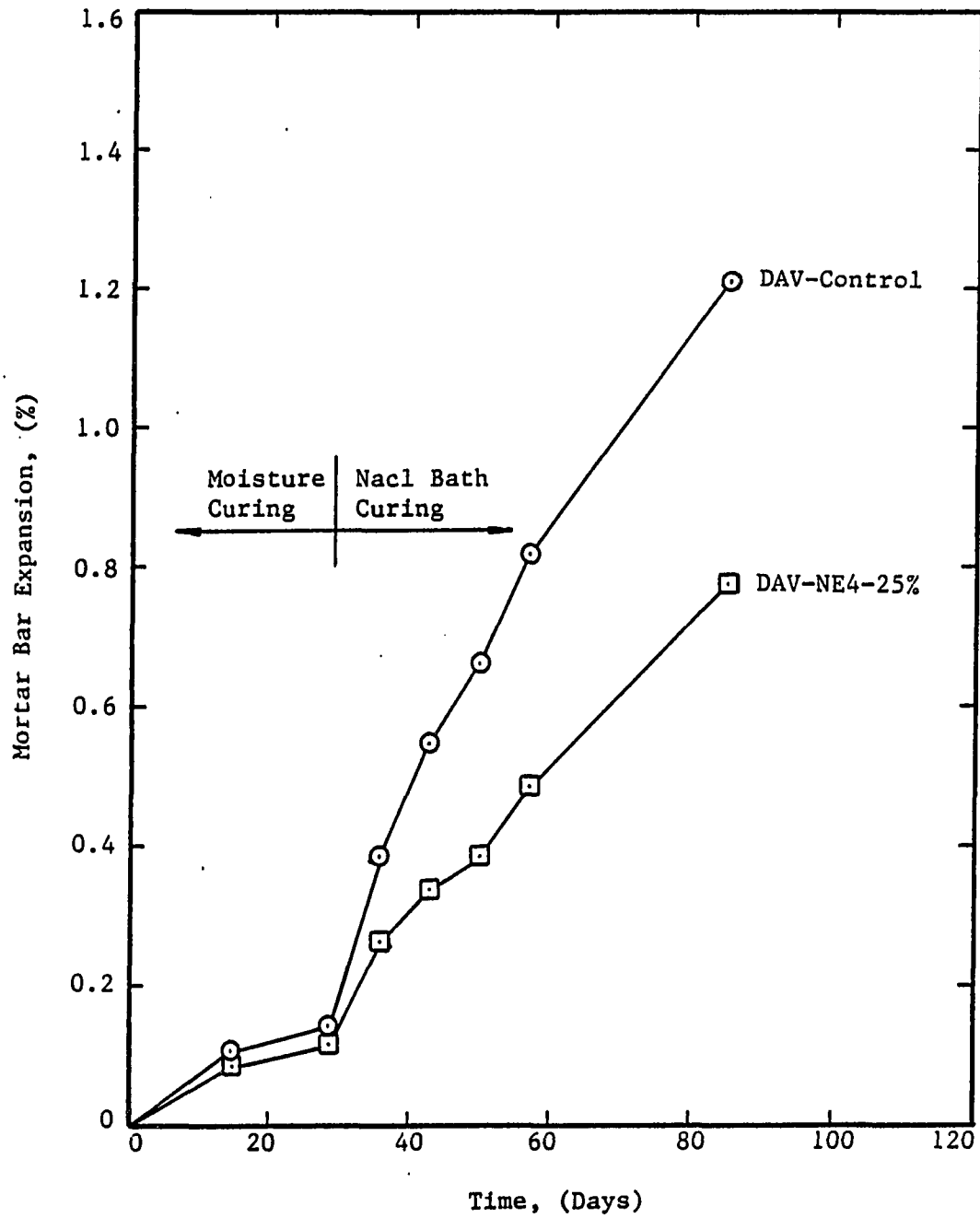
FIGURE 50. Effect of alkalis from external source on expansion of mortar bars containing DAV cement and NE4 fly ash
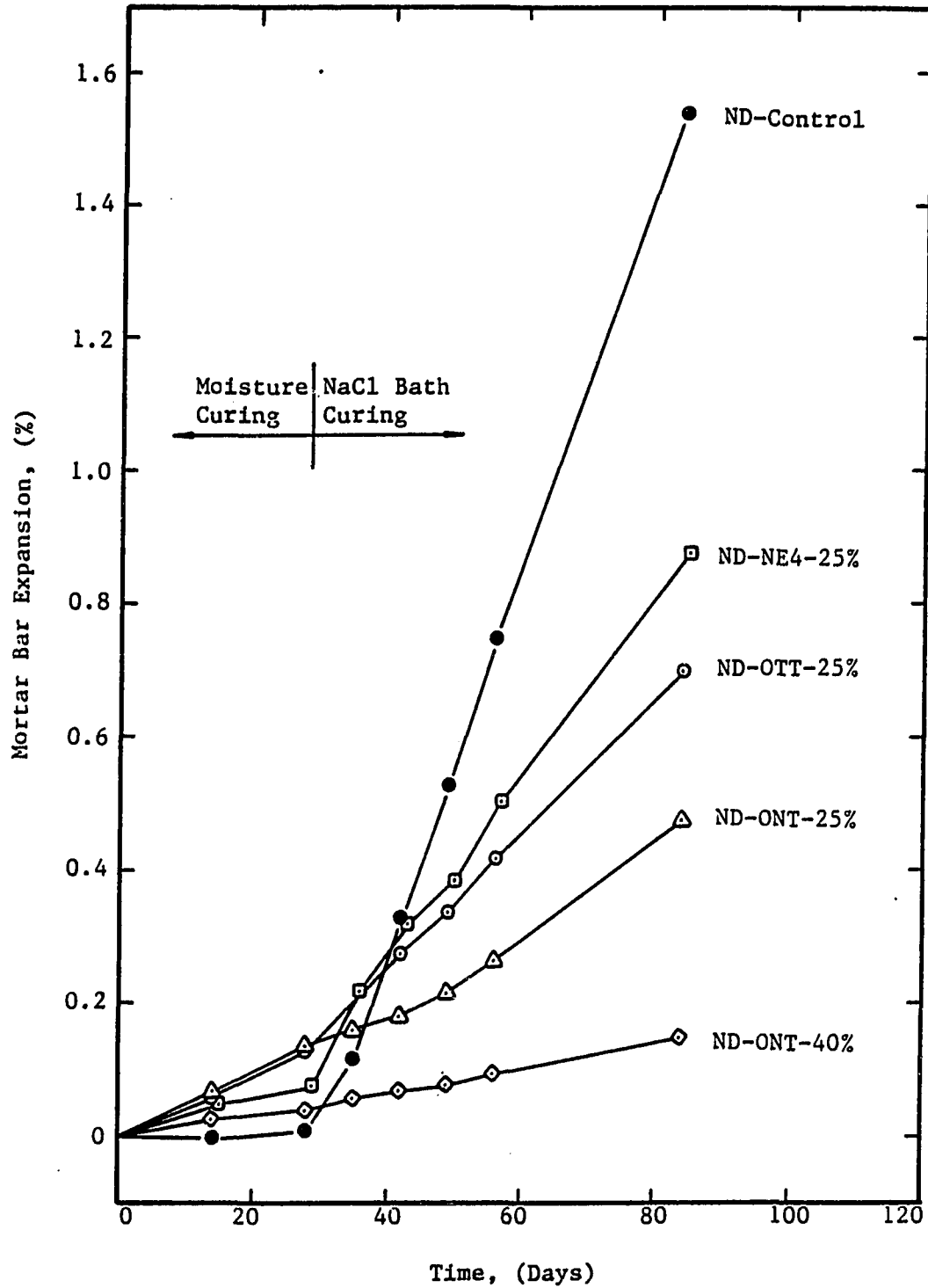
FIGURE 51. Effect of alkalis from external source on
expansion of mortar bars containing ND cement
and Class C fly ashes
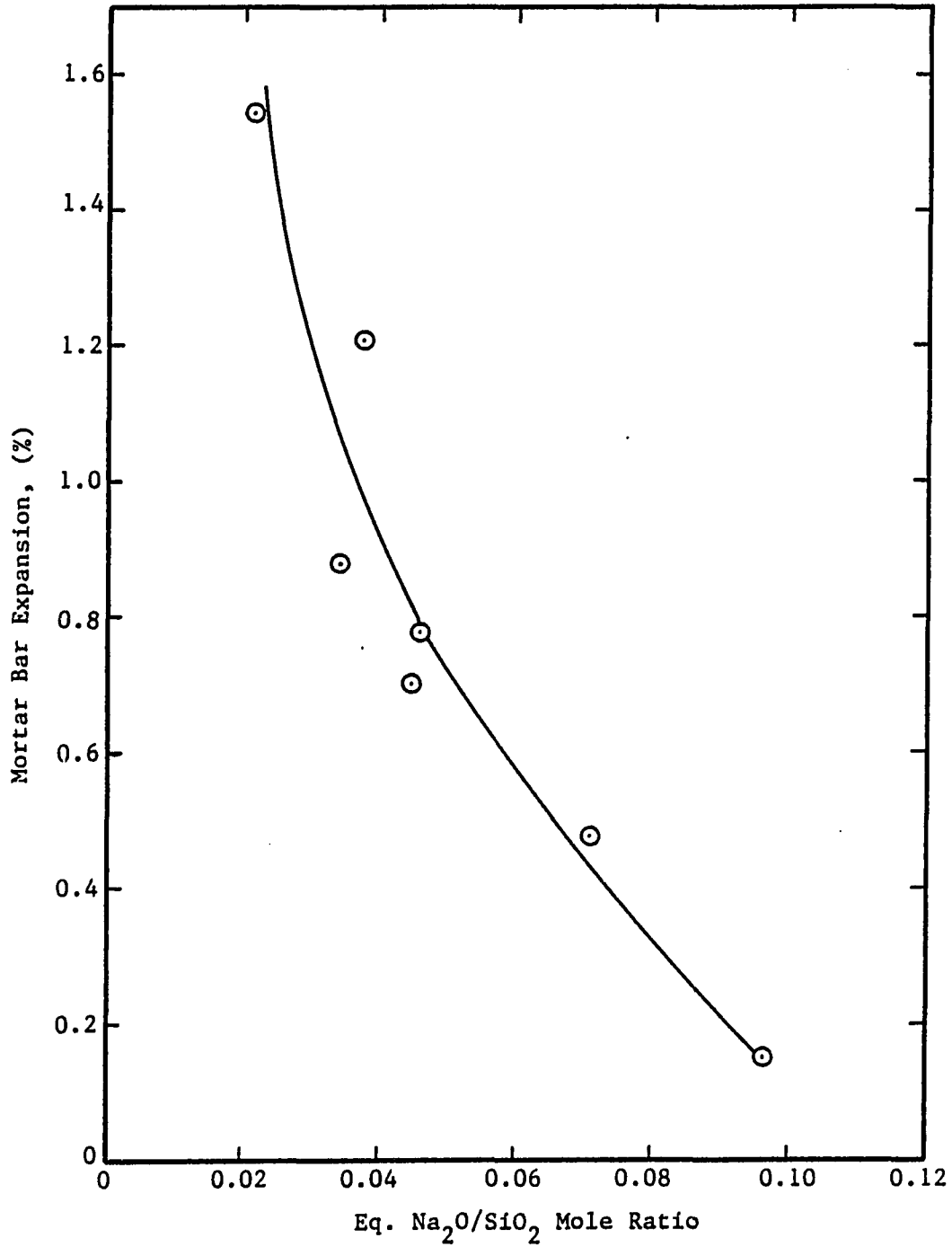
FIGURE 52. Effect of N/S mole ratio in paste on mortar bar expansion when attacked by alkalis from external source

permeability of mortar was also reduced due to replacement by fly ash. The extra alkalis from external sources are expected to first react with amorphous silica contained in fly ash producing less alkalis to react with glass particles. Therefore, replacement of a portion of cement with fly ash gave a certain degree of protection for alkali attack from external sources, and the effectiveness of fly ash depended on the characteristics and composition of fly ash and the percentage of fly ash replacement.

Summary

Effects of alkalis in Class C fly ashes on alkali-silica reaction were studied using procedures listed in ASTM C 441. Expansion of mortar bars prepared using high-alkali cement increased at low replacement levels but decreased at high replacement levels for curing periods up to 12 weeks at 38°C; whereas expansion of mortar bars prepared using low-alkali cement increased at all levels of fly ash replacements up to 40% by volume. Pessimum contents of fly ashes, the fly ash content at which the maximum expansion is observed, were found to be about 15% by volume for high-alkali cement and 25% for low-alkali cement. A hypothesis of critical total equivalent Na_2O/SiO_2 (N/S) mole ratio in the cementitious materials of mortar was proposed to explain the mechanism of variation in expansion of mortar bars containing fly ash. For replacement

of both high and low-alkali cements with each individual fly ash, maximum expansion would be obtained at a critical N/S mole ratio. The critical N/S mole ratio varied with the alkali content and the properties of each fly ash.

It was found that more than 85% of total equivalent alkalis contained in the cementitious materials of mortar tended to be mobilized into the pore solution during hydration to be active for alkali-silica reaction when the CaO/SiO_2 mole ratio in the cementitious materials was greater than 1.75. The concentration of active alkalis, % equivalent Na_2O, was found to increase with increasing N/S mole ratio in the cementitious materials. An empirical regression equation was developed to estimate the active alkali concentration from N/S mole ratio of the cementitious materials.

Because of the complexity of alkali-silica reaction producing amorphous reaction products, no crystalline reaction products could be identified by X-ray diffraction. X-ray diffraction data showed that calcium hydroxide contents of fly ash replaced mortars were reduced with curing time due to pozzolanic reactions. Results of scanning electron microscopy and energy dispersive X-ray analysis showed that the reaction product was an alkali-silicate gel, composed mainly of silica, sodium, potassium, calcium and small amount of aluminum, with their relative amounts varying within the gel. The gel coated the Pyrex glass aggregates and penetrated into the cement

matrix or voids.

The rate and amount of expansion profoundly increased when mortar bars were immersed in saturated NaCl solution at 38°C. However, replacements of a portion of cement with fly ash gave a certain degree of protection for attack of alkalis from external source. Expansions were found to be inversely related to the N/S mole ratio in the cementitious materials.

CONCLUSIONS

Results obtained from this research indicate that the standard available alkali test, described in ASTM C 311, tends to underestimate the ultimate available alkali content that may be extracted from a fly ash-calcium hydroxide paste after long periods of curing at 38°C. It was found that the ultimate concentration of available alkalis in fly ash (or active alkalis in cement-fly ash paste), expressed as % equivalent Na_2O, was a function of the total equivalent Na_2O/SiO_2 (N/S) mole ratio of the reacting system. When SiO_2 content of a cement-fly ash mixture is high (low N/S mole ratio) alkalis are retained in the C-S-H gel and do not become available for reaction with reactive aggregates. The following empirical regression equation relating the active alkali content to the N/S mole ratio of the cementitious materials was developed:

$$\% \text{ Eq. } Na_2O = -0.1486 + 28.6153 \ (N/S)$$

The ultimate amount of available alkalis and the rate of alkali dissolution were found to increase with increasing CaO/SiO_2 mole ratio of the reacting system. It is recommended that further research be conducted on this standard test procedure to explicitly define the influence of the composition of a given reacting system on the measured available alkalis. Until such work is completed three measures are suggested for determining or estimating the available alkalis in fly ash or the active alkalis in the actual cement-fly ash combination.

First, the amount of calcium hydroxide to be used for the test should be determined in accordance with the composition of the job cement and the percentage of fly ash to be used for replacement. In other words, the amount of calcium hydroxide to be used in the test should not be fixed as specified by ASTM but it should be adjusted for each case on the basis of the calcium oxide and silica contents of the proposed cement-fly ash mixture. Secondly, the empirical regression equation developed in this study should be used to estimate the concentration of available alkalis (or active alkalis) from the known Na_2O/SiO_2 mole ratio of the reacting system. Finally, the total alkali content, instead of available alkali content, should be used as a conservative measurement of the alkali content of Class C and borderline Class C-Class F fly ashes.

Replacement of a portion of Portland cement with fly ash is commonly used to reduce concrete expansion caused by deleterious alkali-aggregate reaction. About 15 to 30 percent of Portland cement is frequently replaced by fly ash in many recent concrete constructions. Results obtained from this research indicate that replacement of high or low-alkali cement with a Class C fly ash as a mineral admixture may be dangerous for concrete containing reactive aggregate if fly ash is used arbitrarily. Replacements of small amounts of high-alkali cement and up to 40% of low-alkali cement with Class C fly ashes studied in this research produced greater amount of

mortar bar expansions than expansions produced by plain cement mortar bars. Effect of fly ash on mortar bar expansion is dependent not only upon the percentage of replacement but also upon the composition of the cementitious materials. Maximum expansion may be observed when the total equivalent Na_2O/SiO_2 mole ratio of the cementitious materials is at a critical value. This critical N/S mole ratio seems to vary from fly ash to fly ash.

Until further investigations produce more definite criteria, the author recommends that:

1. Alkali reactivity (mortar bar) tests should be conducted using mixtures with various replacement levels to determine the relationship between expansion and N/S mole ratio. Then a mix corresponding to a safe N/S mole ratio should be recommended for use in the field. If SiO_2 content of the mixes fails to meet these criteria other sources of SiO_2 such as silica fume or Class F fly ash should be incorporated into trial mixes to meet the criteria.

2. Available alkali tests should be conducted using an amount of $Ca(OH)_2$ equivalent to the CaO content of the proposed cement-fly ash combination.

The rate and the amount of expansion can be greatly accelerated and increased by attack of alkalis from external

source, such as de-icing salts or sea water. Replacement of cement with fly ash in concrete can give a certain degree of protection for concrete from external alkali attack. The increased expansion from external alkali attack tends to be inversely related to the N/S mole ratio in the cementitious materials of concrete.

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