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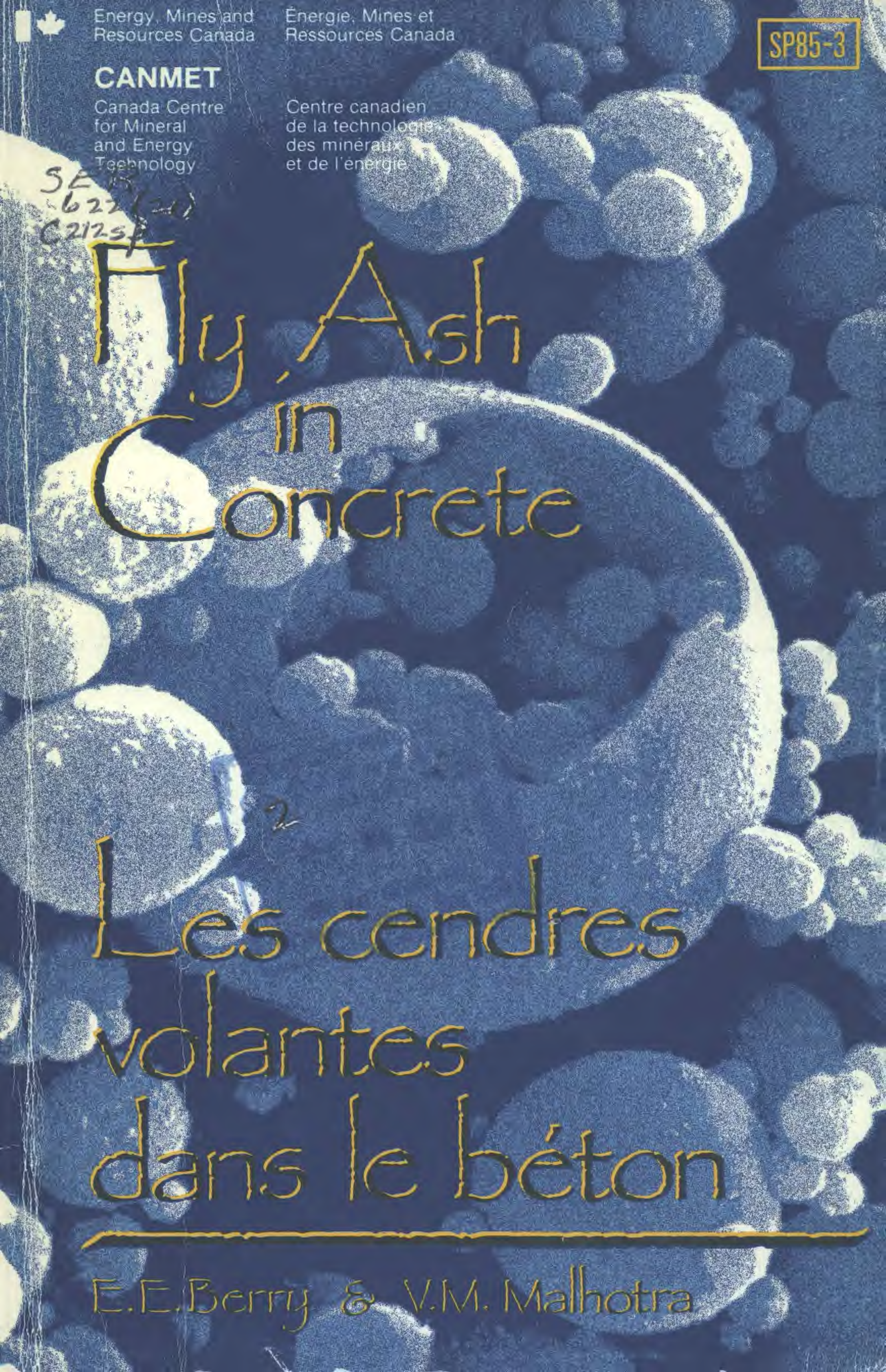

Fly Ash in Concrete

2

Les cendres volantes dans le béton

E.E. Berry & V.M. Malhotra

Cover:
Artist's impression of fly-ash particles

Couverture:
Illustration de particules de cendres volantes

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FLY ASH IN CONCRETE

LES CENDRES VOLANTES DANS LE BÉTON

E.E. Berry

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Mineral Sciences Laboratories/
Laboratoires des sciences minérales

Construction Material Section/
Matériaux de construction

February 1986
Février 1986

SP85-3

Available in Canada through

Authorized Bookstore Agents
and other bookstores

or by mail from

Canadian Government Publishing Centre
Supply and Services Canada
Ottawa, Canada K1A 0S9

Catalogue No. M38-15/85-3 Canada: $7.50

ISBN 0-660-53261-1 Other Countries: $9.00

Price subject to change without notice

PREFACE

The Canada Centre for Mineral and Energy Technology (CANMET), Energy, Mines and Resources Canada, Ottawa, has played a significant role in the research and development of supplementary cementing materials in Canada for over 15 years. In recent years, CANMET has become increasingly involved in research on fly ash in concrete.

In 1976 and 1978, CANMET published reviews of the literature from all over the world on the properties and use of fly ash in concrete. These reviews were well received by industry and the research community. Since the publication of these reviews, a number of conferences and seminars of international scope have been held, and numerous research papers and accounts of fly ash utilization in construction projects have been published. New material combinations, new approaches to old materials, new demands on materials, and new standards have all come to affect the role of fly ash in concrete technology. In view of these changes, and considering the current interest in the use of fly ash, slags, silica fume, and other mineral by-products, it is timely to reconsider some of the issues presented in the previous reviews, to bring up-to-date some of the concepts, and to include issues not previously discussed.

This volume presents a state-of-the-art review of the principal advances in research, development, and practical application of fly ash in concrete that have been made during the period from 1976 to 1984. Recommendations are made with regard to aspects of fly ash concrete technology requiring further research.

It is hoped that this volume will be used by engineers, technologists, and researchers involved in the use of fly ash as a concrete-making material.

W.G. Jeffery
Director General
CANMET
December 1985

PRÉFACE

Pendant plus de quinze ans, le Centre canadien de la technologie des minéraux et de l'énergie (CANMET) a joué un rôle important au Canada dans les activités de R-D portant sur les matériaux de cimentation.

En 1976 et 1978, le CANMET a publié des études documentaires effectuées à l'échelle mondiale sur les propriétés et l'utilisation des cendres volantes dans le béton. Ces études documentaires ont reçu un accueil favorable de la part de l'industrie et du monde des chercheurs. Depuis la publication de ces études, plusieurs conférences et séminaires ont eu lieu au niveau international, et de nombreuses communications sur les recherches portant sur l'utilisation des cendres volantes dans les projets de construction ainsi que des exposés ont été publiés. De nouvelles combinaisons de matériaux et de nouvelles façons d'utiliser les anciens matériaux, de nouvelles exigences pour les matériaux ainsi que de nouvelles normes produisent toutes un effet sur le rôle des cendres volantes dans la technologie de fabrication du béton. En raison de ces changements et de l'intérêt actuel quant à l'utilisation des cendres volantes, des laitiers, de la poussière de silice et des autres sous-produits de minéraux, il semble opportun de réexaminer certains points présentés dans les études documentaires antérieures, de mettre à jour quelques-uns des concepts et d'inclure des sujets qui n'ont pas été traités auparavant.

Ce volume présente donc une étude de l'état actuel des principaux progrès dans le domaine de la recherche, du développement et des utilisations pratiques des cendres volantes dans le béton, réalisés entre 1976 et 1984. Il contient aussi des recommandations quant aux aspects de la technologie des cendres volantes dans le béton nécessitant des recherches plus poussées.

Il est à souhaiter que ce volume sera utilisé par les ingénieurs, les technologistes et les chercheurs effectuant des travaux dans lesquels les cendres volantes entrent comme matériau dans la fabrication du béton.

Directeur général du CANMET
W.G. Jeffery
Décembre 1985

ACKNOWLEDGEMENTS

The authors wish to thank the following individuals for their assistance in reviewing the draft manuscript and for their helpful suggestions.

- Edward A. Adbun-Nur, Consultant, Denver, Colorado, U.S.A.
- G.G. Carette, Materials Engineer, CANMET, Energy, Mines and Resources Canada, Ottawa, Ontario, Canada.
- H.L. Isabelle, Manager, Cement and Concrete Research Laboratory, Technical and Research Centre, Canada Cement Lafarge Limited, Montreal, Quebec, Canada.
- Bryant Mather, Chief, Structures Laboratory, Waterways Experiment Station, Vicksburg, Mississippi, U.S.A.
- P.K. Mehta, Ph.D., Professor, Department of Civil Engineering, University of California, Berkeley, California, U.S.A.

Thanks are also extended to Ms. Sivasundaram for proofreading various drafts of the manuscript.

FOREWORD

This volume presents a state-of-the-art review of the principal advances in research, development, and practical application of fly ash in concrete that have been made during the period 1976 to 1984. Recommendations are made with regard to aspects of fly ash concrete technology requiring further research.

The use of fly ash in concrete has increased worldwide in the past few years. Increased costs for cement have favoured the use of all classes of supplementary cementing materials in concrete for all types of applications.

Low-calcium fly ashes have been used in concrete construction for more than thirty years in North America. As a result of research, advances in understanding the ways in which fly ash influences the properties of fresh and hardened concrete have been extensive during the past decade. This has led to the development of methods of proportioning concrete mixes that permit the use of fly ash in concrete without the disadvantages once considered by some to be inherent in its application. In general, this requires the use of fly ash of fine particle size, low carbon content, and effective pozzolanic reactivity with cement. Fly ash with such characteristics is usually found to reduce water demand, improve workability, and contribute to strength development at a sufficiently early age to be an effective cementitious component of concrete.

Some new uses for fly ash have been reported. High-strength concretes in particular have been found to benefit from the incorporation of fly ash. Much roller-compacted concrete relies for its performance, placement, and cost upon the use of large quantities of fly ash as a substitute for portland cement in very lean mixes.

High-calcium fly ashes have been increasingly studied and are finding application in all types of concrete. The self-cementing activity of these ashes is of some value in many applications and has been exploited where early strength development is required. Presently, relatively little has been reported on the properties of concretes incorporating this class of fly ashes.

With regard to the durability of concretes containing fly ash, there is still disagreement as to the effects of all types of fly ash on sulphate resistance, abrasion, erosion, and alkali-aggregate reactivity of concretes in service. It is now widely accepted that when adequately air-entrained and properly cured, concretes containing fly ash are no less frost-resistant than those without fly ash. Some research has been reported on novel approaches to preventing the increased demand for an air-entraining agent that frequently results from the presence of carbon in some fly ashes.

Interest in the development of very light-weight concrete structures has increased recently particularly for offshore applications. The use of fly ash in conjunction with lightweight aggregate holds promise in this respect, and is an area that needs research and development.

Specifications and codes of practice, as well as testing procedures associated with quality control of fly ash for use in concrete, remain largely inadequate. Research is required into test methods and the applicability of current testing procedures in specifications.

The report is concluded with a list of 224 references.

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February 1986

AVANT-PROPOS

Ce volume présente une étude de l'état actuel des principaux progrès dans le domaine de la recherche, du développement et des utilisations pratiques des cendres volantes dans le béton, réalisés entre 1976 et 1984. Il contient aussi des recommandations quant aux aspects de la technologie des cendres volantes dans le béton nécessitant des recherches plus poussées.

L'utilisation des cendres volantes dans le béton a augmenté à travers le monde au cours des dernières années. La hausse des coûts du béton a favorisé l'emploi de toutes les catégories de matériaux de cimentation supplémentaires dans la préparation du béton servant à tous genres d'utilisation.

Les cendres volantes à faible teneur en calcium ont été utilisées depuis plus de trente ans dans les constructions en béton en Amérique du Nord. Par suite des travaux de recherche, des progrès considérables ont été réalisés au cours de la dernière décennie dans le but de comprendre par quels procédés les cendres volantes influencent les propriétés du béton frais et du béton durci. Ces travaux ont mené à la mise au point de méthodes visant à doser les mélanges de béton dans lesquels les cendres volantes sont utilisées, sans les inconvénients considérés autrefois par certains comme étant inhérents à l'utilisation de ces dernières. Dans l'ensemble, ces méthodes utilisent des cendres volantes de dimension granulométrique fine et à faible teneur en carbone et qui démontrent une réactivité pouzzolanique effective avec le ciment. Les cendres volantes qui possèdent de telles caractéristiques, réduisent habituellement la demande en eau, améliorent la maniabilité et contribuent dès un jeune âge au développement de la résistance du béton; ce qui permet de les utiliser comme un constituant de cimentation efficace du béton.

Certains usages nouveaux pour les cendres volantes ont été présentés. Notamment, les bétons à haute résistance qui semblent avoir bénéficié de l'addition de cendres volantes à leur mélange. Les bétons compressés au rouleau dépendent aussi sur l'emploi des cendres volantes pour leur rendement, leur emplacement et leur coût; les cendres volantes sont utilisées en grandes quantités dans ces bétons comme substitut au ciment Portland dans les mélanges très pauvres.

Les cendres volantes à haute teneur en calcium sont de plus en plus étudiées et on leur trouve de nouvelles applications dans toutes les catégories de béton. L'activité d'auto-cimentation de ces cendres possède une certaine valeur pour de nombreuses applications et a été exploitée dans les cas où le développement de la résistance, dès le début, est nécessaire. Cependant, il y a très peu d'études présentées actuellement sur les propriétés des bétons contenant cette classe de cendres volantes.

En ce qui concerne la durabilité des bétons contenant des cendres volantes, il y a encore une différence d'opinion quant aux effets de tous les genres de cendres volantes sur la résistance du sulfate, l'abrasion, l'érosion et la réaction des agrégats-alcalis des bétons utilisés à l'heure actuelle. Il est maintenant reconnu que bien entraînés à l'air et traités correctement, les bétons contenant des cendres volantes ne sont pas moins résistants au gel que les bétons sans cendres volantes. Certaines recherches portant sur de nouvelles méthodes pour éviter une hausse de la demande d'entraîneurs d'air souvent causée par la présence de carbone dans certaines cendres, ont été présentées.

On manifeste de plus en plus d'intérêt pour la mise au point de structures très légères en béton, tout particulièrement pour des applications au large des côtes. L'emploi de cendres volantes avec des agrégats légers semble prometteur à cet égard, et c'est un domaine qui a besoin de R-D.

Les spécifications et les codes de procédures, ainsi que les méthodes d'essais associés au contrôle de la qualité des cendres volantes utilisées dans la fabrication du béton, sont en grande mesure inadéquats. Il est donc nécessaire d'effectuer des recherches portant sur les méthodes d'essais et l'applicabilité des procédures d'essais actuelles par rapport aux spécifications.

Une liste de 224 références est présentée à la fin de ce rapport.

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Février 1986

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1. INTRODUCTION

"In the real world of modern concrete, fly ash is as essential an ingredient of the mixture as are portland cement, aggregates, water and chemical admixtures. In most concretes, I use it in larger amounts (by volume) than portland cement, and therefore it is not an admixture, i.e., an addition to the mixture. Concrete without fly ash and chemical admixtures should only be found in museum showcases." — E.A. Abdun-Nur, 1984

Fly ash is a by-product of the combustion of pulverized coal in thermal power plants. It is removed by the dust collection system as a fine particulate residue from the combustion gases before they are discharged into the atmosphere.

Fly ash particles are typically spherical, ranging in diameter from less than 1 up to 150 μm, the majority being less than 45 μm. The range of particle sizes in any given fly ash is largely determined by the type of dust collection equipment used. The fly ash from boilers at some older plants, where mechanical collectors alone are employed, is coarser than from plants using electrostatic precipitators.

The chemical composition of fly ash is determined by the types and relative amounts of incombustible matter in the coal used. More than 85% of most fly ashes comprise chemical compounds and glasses formed from the elements silicon, aluminum, iron, calcium, and magnesium. Generally, fly ash from the combustion of subbituminous coals contains more calcium and less iron than fly ash from bituminous coal. Unburned coal collects with the fly ash as carbon particles, the amount being determined by such factors as the rate of combustion, air/fuel ratio, and degree of pulverization of the coal. In general, fly ash from subbituminous coals contains very little unburned carbon. Plants that operate only intermittently (peak load stations), burning bituminous coals, produce the largest percentage of unburned carbon.

Fly ashes exhibit pozzolanic activity. A pozzolan is defined (1) as "a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but which will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties." Fly ashes contain meta-stable alumino-silicates that will react with calcium ions, in the presence of moisture, to form calcium silicate hydrates.

Over 2000 years ago, Roman builders recognized that certain volcanic ashes were capable of combining with lime to form effective cements. This pozzolanic property was widely exploited in ancient construction, and many structures built during the Roman period still remain today. The modern recognition that fly ash is pozzolanic has led to its use as a constituent of contemporary portland cement concrete.

The term *fly ash* was coined in the electrical power industry in about 1930. The first comprehensive data on its use in concrete in North America were reported in 1937 by Davis et al. (2). The first major practical application was reported in 1948 with the publication by the United States Bureau of Reclamation of data on the use of fly ash in the construction of the Hungry Horse Dam. Worldwide acceptance has followed slowly upon these early efforts, and its growth has been particularly noticeable in the wake of the rapid increase in energy costs (and hence cement costs) that occurred during the 1970's.

In 1977, Manz (3) reported the estimated production of coal ash, worldwide, to be 278 443 000 metric tons of which approximately 11.4% was used. Figure 1.1 shows the estimated distribution of production of coal ash in 1977. Table 1.1 shows the estimated percentage of the collected fly ash used in cement and concrete in eight countries as reported in 1982 by Idorn (4).

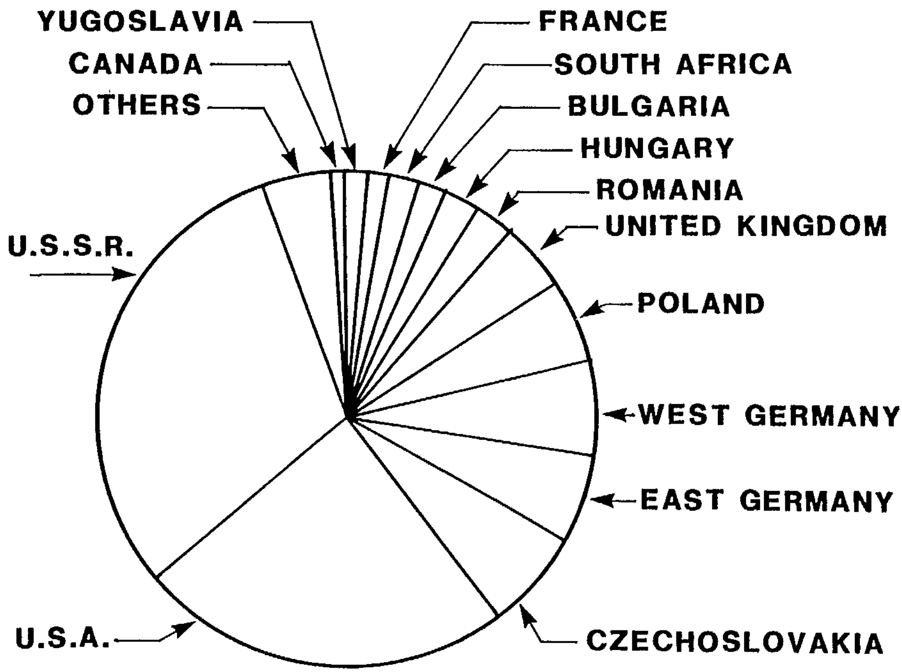

Fig. 1.1 — Distribution of world production of coal ash in 1977 (3). (Total reported: 278 443 000 metric tons)

Table 1.1 — Percentage of collected fly ash used in cement and concrete in eight countries*

Country	% Used	Year
France	24	1978
UK	19	1978
Poland	14	1975
Denmark	14	1981
W. Germany	8-10	1978
Canada**	7	1982
United States	6	1978
India	1	1978

*From reference 4.
**Data for Canada revised to reflect recent usage.

The properties of both freshly mixed and hardened concretes are intimately and complexly associated with the characteristics and relative proportions of the materials used in their manufacture. In fresh concrete, the coarse and fine aggregates are suspended in cement paste. The consistency of the mass is controlled by the fluidity of the paste and the quantity and grading of the aggregate. In hardened concrete, properties such as strength are functions of the density of the paste, which is controlled by the ratio of water to cement in the original mixture. Hence, there are practical limits to the relative proportions of cement, water, and aggregate in normal concretes.

If the aggregates are of satisfactory quality, the performance of concrete in service is primarily influenced by the properties of hardened paste. For a portland cement of given composition, the strength and porosity of the hydrated mass are dependent almost entirely upon the water-to-cement ratio. The lower the ratio, the greater is the strength and the watertightness. Durability in service, or resistance to weathering and attack by aggressive environments, is a function of both strength and watertightness.

The inclusion of fly ash in concrete affects all aspects of concrete properties. As a part of the composite that forms the concrete mass, fly ash acts in part as fine aggregate and in part as a cementitious component. It influences the rheological properties of the fresh concrete, the strength, finish, porosity, and durability of the hardened mass, and the cost and energy consumed in manufacturing the final product.

In recent years, there has been a recognition that fly ashes differ in significant and definable terms, reflecting their composition and, to some extent, their origin. Canadian (5) and U.S. (6) specifications recognize two general classes of fly ash:

- — Class C, normally produced from lignite or subbituminous coals;
- — Class F, normally produced from bituminous coals.

Throughout this review, distinctions will be drawn regarding the behaviour of these two classes of ash that, in many respects, are quite different in the ways in which they function in concrete mixes. The Class C ashes differ from the Class F materials principally in often having a capacity for self-hardening in the absence of cement. The most notable chemical difference between these two classes of ash is that the Class C ashes contain high levels of calcium that has led to the use of an alternative and in some ways preferable terminology: high-calcium and low-calcium ash for Classes C and F, respectively. This terminology has been adopted where appropriate throughout this review. It should be noted that this distinction has not been made in the applicable North American specifications. These presently make no reference to CaO content.

A previous review of the use of fly ash in concrete was published by Berry and Malhotra (7) covering the period from 1960 to 1978. Many significant developments have been reported since then. A number of conferences and seminars of international scope have been held (8-15) and numerous research papers and accounts of fly ash utilization in construction projects have been published. New material combinations, new approaches to old materials, new demands on materials, and new standards have all come to affect the role of fly ash in concrete technology. In view of these changes and in awareness of the current interest in the use of fly ashes, slags, silica fume, and other mineral by-products, the authors feel that it is timely to reconsider some of the issues presented in the previous review, to update some of the concepts, and to include issues not previously discussed.

Wherever possible, while remaining consistent with a critical overview of the subject, emphasis in this report has been placed on recently published material not included in earlier literature reviews by Abdun-Nur (16), Jarriage (17), Snyder (18), Kokubu (19), and Rosner and Hamm (20), each of which remains a valuable source of published material. In some instances, material cited and discussed in the previous review (7) has been omitted or replaced with newer information. This has been done in an endeavour to present material that is as relevant as possible to the current use of fly ash in concrete.

This work has been carried out as part of an ongoing research program at CANMET on the properties and utilization of fly ash, slags, and silica fume in concrete.

2. PROPORTIONING CONCRETES CONTAINING FLY ASH

"Without regard to the actual quantity of mixing water, the following rule is a safe one to follow: Use the smallest quantity of mixing water that will produce a plastic or workable concrete. The importance of any method of mixing, handling, placing and finishing concrete which will enable the builder to reduce the water content of the concrete to a minimum is at once apparent." — Duff A. Abrams, 1918 (21)

In most applications, the objective in using fly ash in concrete is to achieve one or more of the following benefits:

— reducing the cement content to reduce costs;

— obtaining reduced heat of hydration;

— improving workability;

— attaining required levels of strength in concrete at ages beyond 90 days.

In the same manner as other materials, the properties of any particular fly ash will greatly affect the properties of the concrete in which it is used. It is the objective of the mix-proportioning method to minimize the effects of the differences between fly ashes on concrete performance.

In practice, fly ash can be introduced into concrete in one of two ways:

— A blended cement containing fly ash may be used in place of portland cement.

— Fly ash may be introduced as an additional component at the concrete-mixing plant.

The first method is the simpler; it is free from the complications of batching additional materials and more uniform control may be assured. The relative proportions of fly ash and cement are predetermined and, thus, the range of mix proportions is effectively limited.

The second method is flexible and allows for more complete exploitation of the qualities of fly ash as a component of concrete. It does, however, demand that the unique properties of fly ash be considered in determining the mix proportions. The present trend in North American practice is towards the use of fly ash as a separately batched concrete material.

Fly ash plays more than one role in concrete. In the freshly mixed state, it generally acts as a fine aggregate and to some degree may reduce water demand. In the hardened state, because of its pozzolanic nature, it becomes a component of the cementitious matrix and influences strength and durability. Thus, using fly ash in a concrete introduces a number of complexities with regard to proportioning if the accepted relationships between workability, strength, and water–cement ratio are employed.

Two common assumptions are made in selecting an approach to mix proportioning fly ash concrete:

— Fly ash usually reduces the strength of concrete at early ages.

— For equal workability, concrete incorporating fly ash usually requires less water than concrete containing only portland cement.

Neither assumption is universally true and both are influenced by the presence of other commonly used concrete components. However, both assumptions have strongly influenced the ways in which the problem of proportioning concrete mixes to incorporate fly ash has been approached.

As with any other type of concrete, the mix proportions for a fly ash concrete can be selected either by reference to some *standard* non-fly ash concrete, or on the basis of knowledge of the ways in which all of the concrete components (including fly ash) will behave in the fresh and hardened states.

Throughout the more than 40 years during which fly ash has been used in concrete, it has been the more common practice to refer the mix proportions of fly ash concretes to some reference plain concrete. Similarly, the properties in both the fresh and hardened conditions were usually compared with a reference concrete. Thus, fly ash was generally thought of as replacing cement rather than being a component that complements the functions of other components, in particular the cement, sand, and water. Recently, there has been a trend to consider the components of fly ash concrete as a whole and to treat it as a unique material without reference to an "equivalent plain concrete mix." As a consequence of these different ways of thinking about fly ash in concrete, three basic mix-proportioning approaches have developed:

— partial replacement of cement — The Simple Replacement Method;

— addition of fly ash as fine aggregate — The Addition Method;

— partial replacement of cement, fine aggregate and water —

a) the Modified Replacement Method;

b) the Rational Proportioning Approach.

Simple Replacement Method

The Simple Replacement Method requires a direct replacement of a portion of the portland cement by fly ash (22). Much research has shown that any percentage replacement of portland cement in concrete by fly ash on a one-for-one basis (either by volume or by mass) results in lower compressive and flexural strengths up to about three months of moist curing, with the development of greater strengths beyond six months. In mass-concrete applications, where fly ash first came into use, this reduced early strength was of little structural consequence when considered in the light of the desired reduction in temperature rise; replacement methods of mix proportioning were generally used.

The general form of strength development in fly ash concrete when partial replacement of cement is used, is shown graphically in Figure 2.1. The general behaviour of the system is consistent with the view that at early ages fly ash exhibits very little *cementing value* and acts rather as a fine aggregate; at later ages cementing activity becomes apparent and a considerable contribution to strength may result. In this regard, high-calcium fly ashes differ greatly from low-calcium ashes, as is discussed in some detail in Chapter 4 of this report.

Addition Method

In the Addition Method, fly ash is added to the mix without a corresponding reduction in the quantity of cement used. The effective cementitious content of the concrete (especially after long periods of moist curing) is increased by this method. Other mix adjustments are usually made through changes in aggregate content and depend on the nature of the particular job.

An example of this approach comes from the investigation of concrete materials for the construction of the South Saskatchewan River Dam made by Price (23). For reasons of sulphate resistance, it was considered important to use a minimum cement factor and to use pozzolan as a replacement for fine aggregate rather than for cement. It was found that addition of fly ash generally produced increased strength in concrete at all ages. Improvements were small at seven days but ranged up to 6.9 MPa at three months and one year. In some cases, improvements were equal to, or greater than, those obtained by an equal addition of cement. In contrast to fly ash, the addition of pumicite resulted in reduced strengths at all ages.

The third method developed for proportioning fly ash concrete requires a part of the cement to be replaced with an excess by mass of fly ash, with adjustments made in fine aggregate and water content. The method has two variants. In its original form, it has been termed the Modified Replacement Method; in recent practice developments have led to so-called Rational Proportioning Methods.

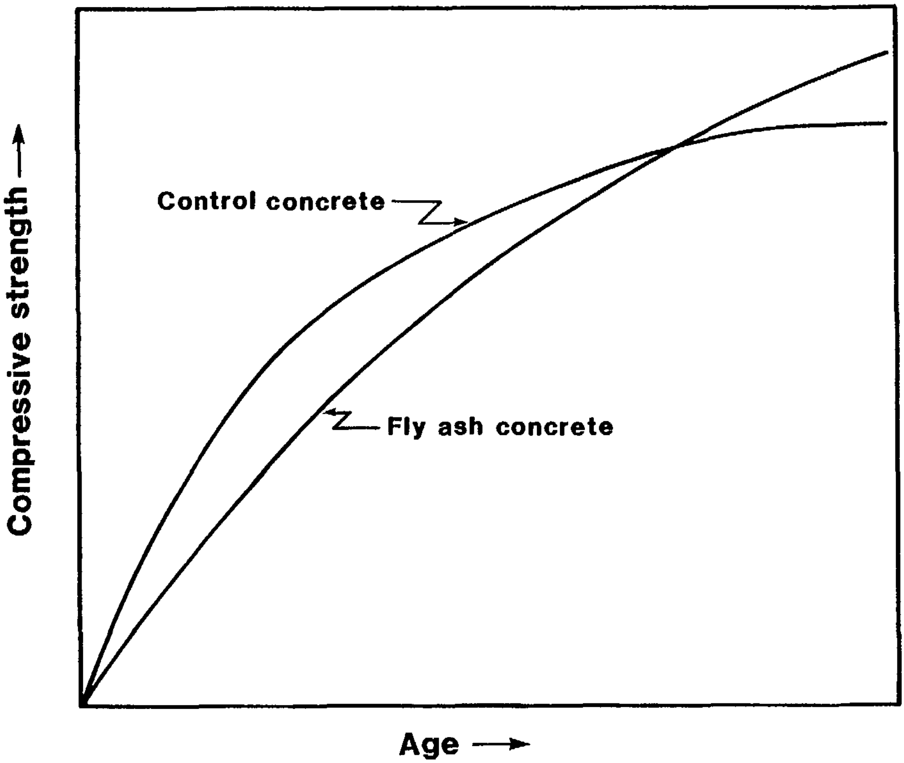

Fig. 2.1 — Relative rates of strength increase of plain concrete and fly ash concrete proportioned by simple replacement of cement

Modified Replacement Method

The Modified Replacement Method probably originated in 1958 with the work of Lovewell and Washa (24) who showed that by modification of mix proportions, fly ash concretes could be made that had strengths at early ages comparable with those of control mixes.

The main point of their conclusions was:

> *"In order to obtain approximately equal compressive strengths at early ages, between 3 and 28 days, mixes made with fly ash must have a total weight of portland cement and fly ash greater than the weight of the cement used in the comparable strength portland cement mixes."*

In the early 1960's it was realized that, if fly ash concrete were to comply with the normally specified requirements of workability and strength, then the characteristics of fly ash most affecting those properties must be accounted for in proportioning mixes. This realization has resulted in the development of several methods of proportioning that are based upon Abrams' relationship between strength and water-to-cement ratio.

Rational Proportioning Approach

Smith (25) was probably the first to propose a rational method of proportioning fly ash concrete. He modified the conventional mix-proportioning procedure to obtain values for cement content and water-to-cement ratio through the introduction of a "fly ash cementing efficiency factor" (k). This factor was assumed to be unique for each fly ash and could be determined from the performance of fly ash concrete mixes or from an initial testing program.

The cementing efficiency factor was defined such that a mass of fly ash (F) was equivalent to a mass (kF) of cement. The required strength and workability of fly ash concrete are then considered to be controlled by the volume ratios of cement-sized particles to water and aggregate, and by the relationship between strength and the ratio of water content to total *cementing material*: $W/(C+kF)$.

The method was applied in Britain, and charts were prepared to simplify proportioning procedures (26). However, as Munday et al. (27) have noted, the approach has certain weaknesses in practice.

1. The value for k is not constant for any particular fly ash. It varies depending upon the cement used (28), the curing conditions employed (29,30), and the nominal strength level to which the concrete is being proportioned (31).
2. The differences in water demand between cement and fly ash and between different fly ashes, cause adjustments to be required to the aggregate content to achieve the desired workability. This was considered to be impractical because, in construction practice, water content is usually adjusted, thus increasing the variability of the strengths attained.
3. The method is complex and probably impractical for most purposes.

Attempts to develop proportioning methods for fly ash concrete based upon Abrams' relationship have been proposed by a number of authors in the context of North American concrete practice.

In 1968, Cannon (32) reported research carried out by the Tennessee Valley Authority on methods of proportioning fly ash concrete mixes to obtain strengths at 28 and 90 days equal to those of conventional control mixes. Cannon employed Abrams' relationship between water-to-cement ratio and strength, and introduced a factor that took account of the relative costs of fly ash and portland cement. This approach, combined with extensive laboratory investigations and field experience, allowed him to develop tables and graphs to facilitate proportioning procedures.

Just as Lovewell and Washa (24) had advocated, Cannon's approach results in the use of a combined mass of portland cement and fly ash greater than the mass of the cement used in a comparable control mix. Cost savings using this method rest upon a significantly lower cost for fly ash than for portland cement.

Rosner (33) outlined a further procedure incorporating some of the concepts from Cannon (32) and from Smith (25).

In 1975, Ghosh (34) further extended the approaches developed by Lovewell and Washa, and by Cannon. Ghosh published a series of empirical relationships which considerably simplified the mix proportioning of fly ash concrete. Using the basic Abrams' relationship that the strength of a fully compacted concrete is inversely proportional to the water-to-cement ratio, which he extended to include the water-to-(cement + fly ash) ratio, Ghosh equated the strengths of fly ash and control concretes in the form:

$$R' = M + NR$$

where:

R = water-to-cement ratio of the control (no fly ash) concrete;

R' = water-to-(cement + fly ash) ratio of the fly ash concrete;

M and N are constants.

Using extensive test results from measurements made in the laboratory, from which the empirical constants M and N were calculated for different ratios of fly ash to cement at selected ages, Ghosh developed a procedure using tables and graphs (Fig. 2.2) from which mix proportions could be selected.

More recently, Popovics (35) has used data from Ghosh's work to develop empirical expressions relating strength and mix proportions for fly ash concrete.

In 1981, the American Concrete Institute published a revised "Standard Practice for Selecting Proportions for Normal, Heavyweight and Mass Concrete" (ACI 211.1-81) (36) that included guidelines for proportioning pozzolan concrete. Two approaches were taken: use of equivalent mass of cementitious material; and use of equivalent absolute volume of cementitious material. Whichever of these approaches is taken, the resulting mix is effectively proportioned by the simple replacement method.

In respect of the known behaviour of fly ash in concrete mixes, using a simple replacement approach can be expected to lead to reduced strength at least until 28 days and probably to much later ages. It is perhaps significant that the literature cited in the Report of ACI Committee 212.1R-13 (37), "Admixtures for Concrete," contains no reference to original research work published after 1968. It should be recognized that much of the early work was conducted using high-carbon, coarse particulate, Class F fly ashes from older power plants. Much of the currently available fly ash, and certainly the ash that will become available in the future as coal-burning power generation expands, comes from modern power plants with high-efficiency combustion, dust removal, and coal pulverization equipment (many burning subbituminous coals). Most of the problems experienced with the use of fly ash during the period from 1950 to 1970 will no longer be relevant to modern concrete practice.

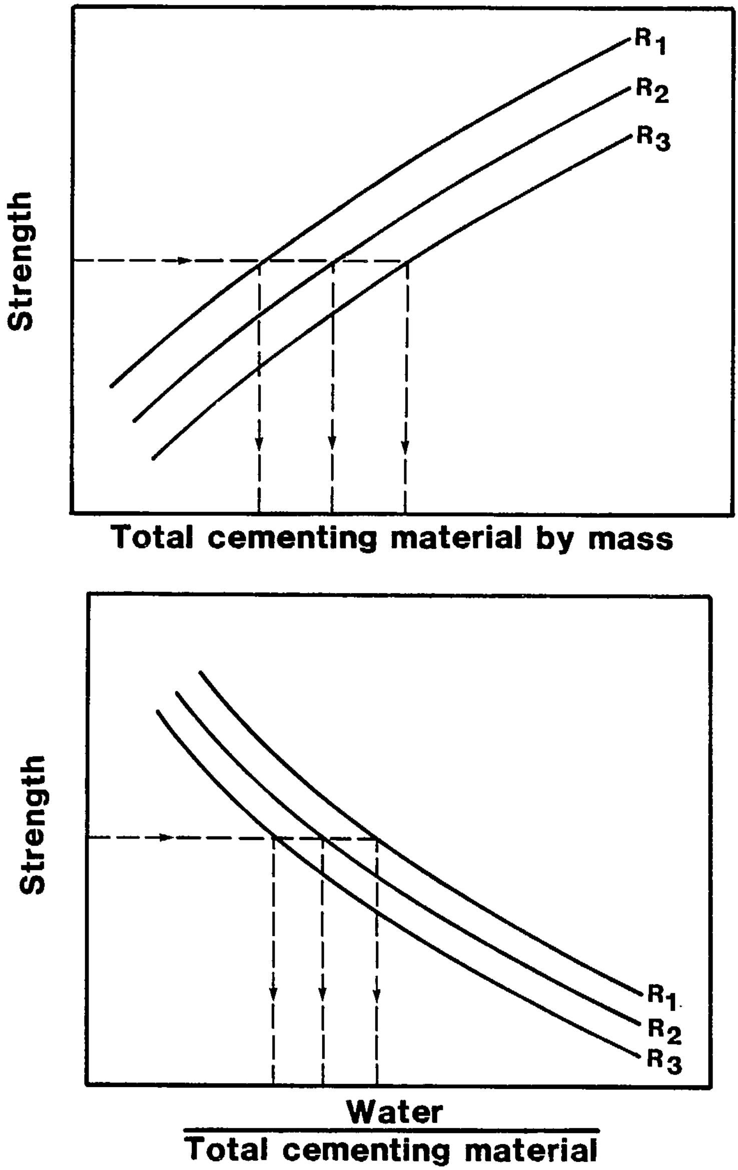

Fig. 2.2 — Strength relationships at any age for different blends of cementing materials (5).

R = ratio of supplementary cementing material to portland cement

In 1982, a National Standard was issued in Canada for supplementary cementing materials and their use in concrete construction (5). In addition to standardizing practice with regard to fly ash use in concrete, the Standard presents guidelines for proportioning fly ash concrete. The approach is based upon the method developed by Ghosh (34).

In Britain, Munday et al. (27) have proposed a procedure for the proportioning of fly ash concrete to obtain any desired strength at 28 days (or at earlier ages if desired). The method requires the collection of data for a fly ash source such that the following six steps can be followed when selecting mix proportions:

- — determination of water-to-cement ratio;
- — selection of *free-water* content;
- — determination of fly ash-to-cement ratio;
- — determination of cement and fly ash content;
- — determination of total aggregate content;
- — examination of trial mixes.

Examples of the mix proportions of a portland cement concrete proportioned by standard methods, and the corresponding fly ash concretes proportioned by the proposed method (using six fly ashes), are given in Table 2.1.

In principle, the recently introduced mix proportioning methods discussed above have demonstrated that it is possible to proportion fly ash concretes to have strength at any desired age equal to, or in excess of, that of comparable, conventional concretes (Fig. 2.3). However, a number of factors must be considered when these approaches are used in practice:

- — As in a normal mix-proportioning procedure, trial mixes must be made, and the concrete components must be adjusted. Additionally, because each fly ash has unique characteristics, knowledge of each fly ash must be developed as an aid to trial mix proportioning.
- — To truly estimate the economic advantages offered by these mix proportioning methods, allowance should be made for the handling of an extra component when fly ash is used as an admixture and batched separately. Such allowances are not made in the procedures outlined above.
- — Concretes made with fly ash are more sensitive to temperature and moisture conditions during curing than are plain concretes. These factors must be considered when data from trial mixes are used to proportion concrete for construction.

Table 2.1 — Mix proportions of control and fly ash concretes proportioned for equal strength at 28 days*

	Fly ash			Mix proportions, kg/m³			
	Source	Retained on 45 μm, %	LOI, %	Cement	Ash	Water	Aggregate
Control concrete	—	—	—	310	—	190	1890
Fly ash concrete	A	11.7	2.3	223	149	166	1838
	B	22.7	4.1	249	159	182	1740
	C	45.7	7.4	298	156	200	1666
	F	25.6	9.5	296	177	210	1612
	G	29.7	5.1	246	163	184	1752
	H	3.3	2.4	215	144	161	1875

*From reference 27.

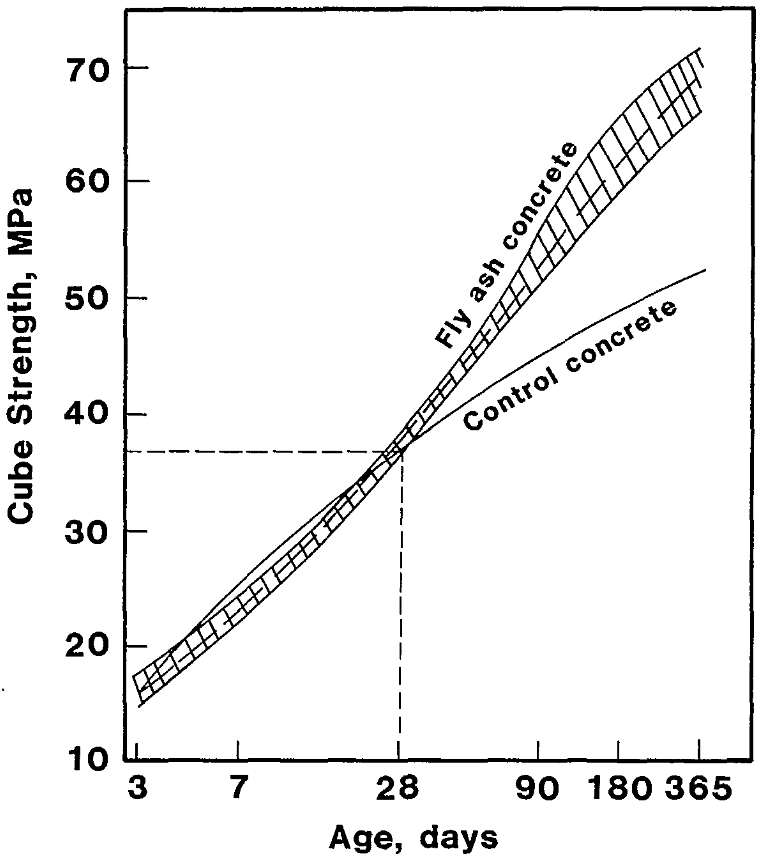

Fig. 2.3 — Strength-age relationship of control and fly ash concrete (27)

3. EFFECTS OF FLY ASH ON PROPERTIES OF FRESH CONCRETE

"A concrete mixture may be so designed that when it is discharged from the mixer it is bulky and nonplastic and remains so during handling. When so designed, it can be molded only by pressure, tamping, or vibration, and in the process it does not become plastic. Compacting and molding such a mixture involves overcoming internal resistance to movement of one part of the material with respect to another part, and thus it involves internal strain and stress."
— Treval C. Powers, 1968.

Fresh concrete is a concentrated suspension of particulate materials of widely differing densities, particle sizes, and chemical compositions in a solution of lime and other components. The system is not static. As soon as the cement and water mix, reactions commence that ultimately produce the binder that consolidates the concrete mass. New particles are formed, and original particles dissolve or are coated with cementitious products. The forces of dispersion, flocculation, and gravity compete to determine the spatial distribution of the materials in the changing mass. Heat is released during the chemical reactions and the temperature rises. In all of these events fly ash plays some role. Low-calcium fly ash will act largely as a fine aggregate of spherical form, high-calcium fly ash on the other hand may participate in the early cementing reactions, in addition to being part of the particulate suspension.

Because concrete must be mixed and placed, frequently in heavily reinforced formwork, it is necessary that in most cases a level of fluidity, generally termed workability, be maintained. This is determined by the rheological properties of the system that are influenced by all of the components. Control of workability is one of the objectives of mix proportioning.

Therefore, it is essential to understand the role of fly ash in the rheology of fresh concrete if the optimum exploitation of its properties is to be made.

In practical terms, the fluidity of concrete is expressed in such phenomenological measurements as workability, compactability, pumpability, water demand, and bleeding. As the use of fly ash has increased, a gradual understanding of its role in determining these properties has started to form. This chapter is largely concerned with these issues and with the other important properties of fresh concrete: temperature rise and air-entrainment.

Recent work at CANMET (38) illustrates some of the effects of fly ash on the general properties of fresh concrete. The study concerned the examination of eleven fly ashes from widely different sources in Canada. The chemical and physical properties of these ashes are given in Table 3.1. A number of air-entrained concretes have been prepared using simple replacement of cement

Table 3.1 — Properties of some Canadian fly ashes*

Fly ash Source	Type of Coal**	Chemical composition***, weight per cent												
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	BaO	SO_3	LOI****
1	B	47.1	23.0	20.4	1.21	1.17	0.54	3.16	0.85	0.16	0.78	0.07	0.67	2.88
2	B	44.1	21.4	26.8	1.95	0.99	0.56	2.32	0.80	0.27	0.12	0.07	0.96	0.70
3	B	35.5	12.5	44.7	1.89	0.63	0.10	1.75	0.56	0.59	0.12	0.04	0.75	0.75
4	B	38.3	12.8	39.7	4.49	0.43	0.14	1.54	0.59	1.54	0.20	0.04	1.34	0.88
5	B	45.1	22.2	15.7	3.77	0.91	0.58	1.52	0.98	0.32	0.32	0.12	1.40	9.72
6	B	48.0	21.5	10.6	6.72	0.96	0.56	0.86	0.91	0.26	0.36	0.21	0.52	6.89
7	SB	55.7	20.4	4.61	10.7	1.53	4.65	1.00	0.43	0.41	0.50	0.75	0.38	0.44
8	SB	55.6	23.1	3.48	12.3	1.21	1.67	0.50	0.64	0.13	0.56	0.47	0.30	0.29
9	SB	62.1	21.4	2.99	11.0	1.76	0.30	0.72	0.65	0.10	0.69	0.33	0.16	0.70
10	L	46.3	22.1	3.10	13.3	3.11	7.30	0.78	0.78	0.44	0.13	1.18	0.80	0.65
11	L	44.5	21.1	3.38	12.9	3.10	6.25	0.80	0.94	0.66	0.17	1.22	7.81	0.82

*From reference 38.
**B: Bituminous; SB: subbituminous; L: lignite.
***Inductively Coupled Argon Plasma (ICAP) Technique, except for Na_2O, K_2O, SO_3 and LOI.
****Between 105 and 750°C.

and proportioning the mixes to obtain equal ratios of water-to-(cement + fly ash) at a fixed total cementitious materials content. Table 3.2 shows the mix proportions used and the properties of the fresh concretes obtained.

In general, it is clear that, at a fixed water-to-(cement + fly ash) ratio, slump does not always increase with the incorporation of fly ash. Another important factor revealed by this work is that the amount of air-entraining admixture required to provide 6% air varied greatly from one ash to another, and was not always in excess of the quantity required by the control concrete. Both of these issues are discussed in detail elsewhere in this chapter.

Table 3.2 — Mix proportions and properties of concretes incorporating some Canadian fly ashes*

	Batch quantities, kg/m³						Cement replacement by fly ash
			Aggregate				
Mix No.***	Cement	Fly ash	Fine	Coarse	AEA, mL/m³	W/(C+F)**	% by mass
Control	295	0	782	1082	170	0.50	0
F1	236	59	780	1077	320	0.50	20
F2	237	59	782	1080	200	0.50	20
F3	237	59	786	1088	200	0.50	20
F4	238	59	792	1094	160	0.50	20
F5	237	59	782	1080	690	0.50	20
F6	238	59	784	1082	660	0.50	20
F7	239	59	780	1077	370	0.50	20
F8	236	59	775	1069	230	0.50	20
F9	236	59	775	1070	240	0.50	20
F10	237	59	781	1079	290	0.50	20
F11	237	59	782	1080	150	0.50	20

					Setting time, h:min	
Mix No.	Slump mm	Air %	Unit wt. kg/m³	Bleeding, %	Initial	Final
Control	70	6.4	2320	2.9	4:10	6:00
F1	100	6.2	2300	3.1	4:50	8:00
F2	105	6.2	2310	4.6	7:15	10:15
F3	100	6.2	2310	5.1	5:20	8:10
F4	110	6.3	2320	4.3	6:20	8:25
F5	65	6.4	2310	2.7	5:15	8:55
F6	75	6.5	2300	2.6	4:30	6:50
F7	100	6.1	2300	2.9	4:15	6:20
F8	115	6.2	2300	5.6	5:10	7:30
F9	100	6.4	2280	4.4	5:25	9:00
F10	130	6.5	2290	2.5	4:45	7:00
F11	140	6.6	2290	0.6	4:00	6:05

*From reference 38.
**Water-to-(cement + fly ash) ratio by mass.
***Mix numbers correspond with fly ash numbers in Table 3.1.

Influence of Fly Ash on the Setting Time of Portland Cement Concrete

The rate at which concrete sets during the first few hours after mixing is expressed as initial and final setting time, and is determined by some form of penetrometer test.

It may be expected that fly ash would influence the rate of hardening of cement for one or more of a number of reasons:

- The ash itself may be cementitious (high-calcium).
- Fly ash may contain sulphates that react with cement in the same way as does the gypsum added to portland cement.
- The fly ash–cement mortar may contain less water as a consequence of the presence of fly ash, and this will influence the rate of stiffening.
- The ash may absorb surface-active agents added to modify the rheology (water reducers) and again influence stiffness in the mortar.
- Fly ash particles may act as nuclei for crystallization of cement hydration products (39).

There seems to be general agreement in the literature that low-calcium fly ashes show a degree of retarding influence on cement setting. In experiments conducted at CANMET (38), the data obtained (see Table 3.2) show that all except one of the eleven ashes examined significantly increased both the initial and final setting times. Fly ashes with CaO content ranging from 1.4 to 13.0% were included in this study.

Lane and Best (40) state that fly ash generally slows the setting of concrete. They conclude that the observed retardation may be affected by the proportions, fineness, and chemical content of the ash; however, the cement fineness, the water content of the paste, and the ambient temperature are considered to have a much greater effect.

Davis et al. (2) concluded that fly ash-cement mixes set more slowly than corresponding cements, but that the setting times were within the usual specified limits.

Mailvaganam, Bhagrath, and Shaw (41) examined a number of properties of fresh and hardened concretes made at two temperatures, with a low-calcium fly ash, in the presence of various admixtures. Data from their study are shown in Table 3.3. Concretes mixed at 5°C showed retardation to give setting times in excess of 10 h, regardless of fly ash content. Concretes mixed at 20°C, and containing 30% of fly ash (by weight of cement) showed setting times extended by approximately 1 to 1.75 h.

Table 3.3 — Properties of fresh fly ash concretes*

Mix**	Admixture***	Slump mm	W/C	Bleeding %	Entrapped air %	Initial set h:min
1	—	90	0.56	3.97	3.3	4:35
2	—	90	0.60	4.93	1.7	5:25
3	CL	70	0.55	3.09	3.3	4:35
4	CL	90	0.58	3.19	3.0	5:25
5	MFS	75	0.51	1.61	3.2	4:25
6	MFS	90	0.55	2.52	2.5	5:20
7	NCL	80	0.55	3.38	3.0	5:00
8	NCL	90	0.58	3.91	1.9	5:45
9	—	80	0.57	6.09	3.6	>10:00
10	—	85	0.59	7.24	2.2	>10:00
11	CL	85	0.57	3.87	3.3	>10:00
12	CL	90	0.57	4.86	3.5	>10:00
13	MFS	70	0.50	0.47	3.8	>10:00
14	MFS	90	0.51	1.26	3.1	>10:00
15	NCL	75	0.53	1.97	3.7	>10:00
16	NCL	85	0.56	5.09	2.6	>10:00

*From reference 41.
**Mixes 1 to 8 made at 20°C; 9 to 16 made at 5°C.
***CL = Chloride accelerator (1.5% active solids)
MFS = Superplasticizer (0.6% active solids)
NCL = Non-chloride accelerator (0.68% active solids)
All at a dosage of 3% by weight of cementitious material.

Dodson (42) has sought to separate the chemical from the physical influences that fly ash might have on the setting of concrete. He observes that in concrete not containing fly ash, all conditions being equal, the setting time should be a function of two parameters:

— the cement factor

— the water-to-cement ratio.

As the cement factor increases, the setting time decreases; as the water-to-cement ratio increases, the setting time increases.

Dodson proposes the use of a factor (which he terms the Omega Index Factor (OIF)) expressing the combined influence of these two parameters in the form:

$$\text{OIF} = \frac{\text{cement factor}}{\text{water-to-cement ratio}}$$

Dodson reported setting time determinations for 19 concrete mixes, of which four contained low-calcium fly ashes, one contained high-calcium fly ash, and cements of three different origins were used.

A relationship of the general form:

$$\text{Setting time} = B - A \times OIF$$

was found to describe the behaviour of the control concretes, where constants A and B varied considerably from one cement to another. Concretes containing low-calcium fly ash were found to follow the same relationship as was applicable to the cement for which fly ash was substituted. Concretes containing high-calcium fly ashes deviated towards reduced setting times, indicating an accelerating effect.

In summary, the following conclusions can be drawn from this work:

- Initial and final setting times are influenced by the water-to-cement ratio and the total cement content of the concrete. The effects can be represented by a relationship to OIF.
- The relationship between setting times and OIF of concretes made from different cements, while each following the same general form, differs from one another considerably.
- Whereas measured setting times for concretes containing low-calcium fly ashes are extended, the extended setting time is ascribed to the secondary influences of dilution of the portland cement content.
- The one high-calcium fly ash examined by Dodson (25.5% CaO) had a strong influence on setting time, causing a reduction. This may be ascribed to the inherent hydraulic characteristics of this particular ash, a property exhibited by many subbituminous ashes.

The observation of reduced setting time in the presence of high-lime fly ashes is by no means general. Ramakrishnan et al. (43) studied the setting time of mortars from concretes made with Type I and Type III cements with and without fly ash (20.1% CaO). The data from their study are shown in Figure 3.1. It is clear that in the presence of high-lime fly ash, setting was retarded for both types of cements with the effect being minimal for Type III cement.

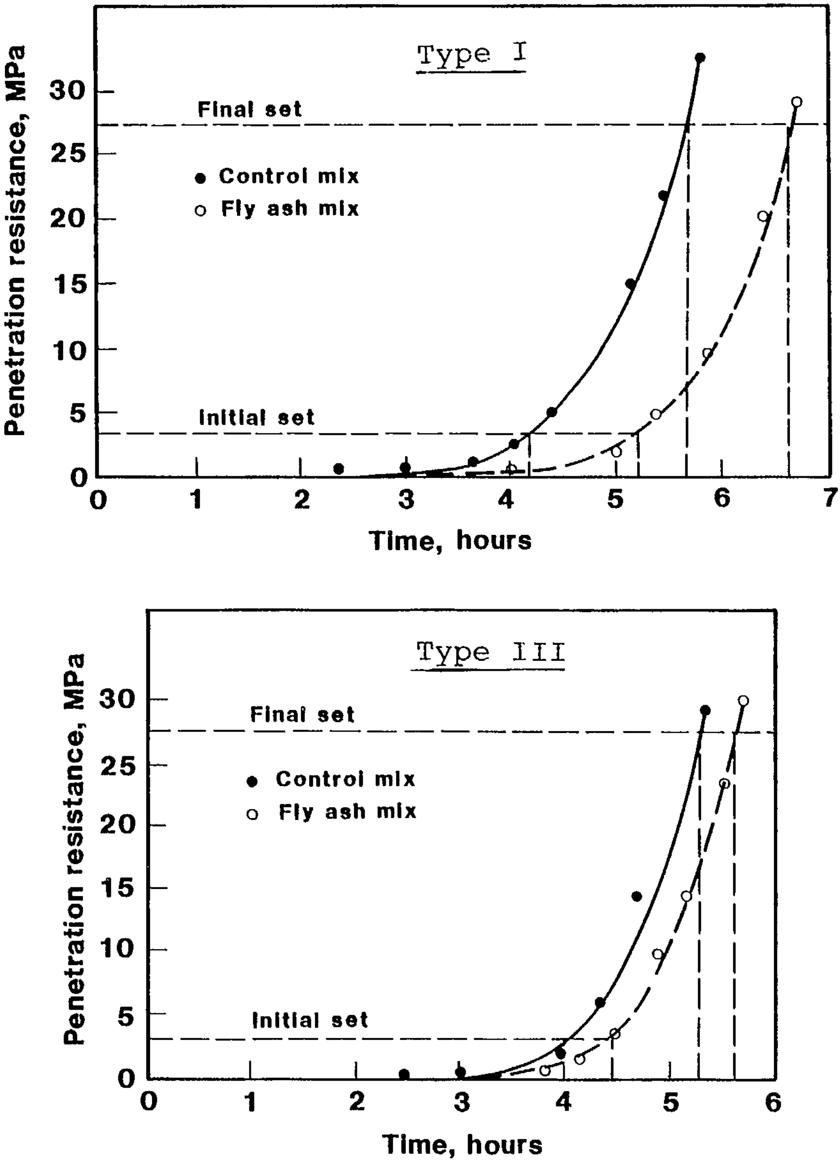

Fig. 3.1 — Comparison of setting time of control and fly ash concretes (43)

Effect of Fly Ash on Workability, Water-Requirement, and Bleeding of Fresh Concrete

The small size and the essentially spherical form of low-calcium fly ash particles have been credited with influencing the rheological properties of cement pastes; this causes a reduction in the amount of water required for a given degree of workability from that required for an equivalent paste without fly ash. In this respect, as noted by Davis et al. (2), fly ash differs from other pozzolans that usually increase the water requirement of concrete mixes. Advantage can be taken of the improved workability to reduce the amount of water used in a concrete and yet maintain the same workability as non-fly ash concrete.

According to Owens (44), the major factor influencing the effects of ash on the workability of concrete is the proportion of coarse material (>45 μm) in the ash. He has shown that, for example, substitution of 50% by mass of the cement with fine particulate fly ash can reduce the water demand by 25%; a similar substitution using ash with 50% of the material greater than 45 μm has no effect on water demand. The general effect of coarse fly ash particles on the water demand is illustrated in Figure 3.2.

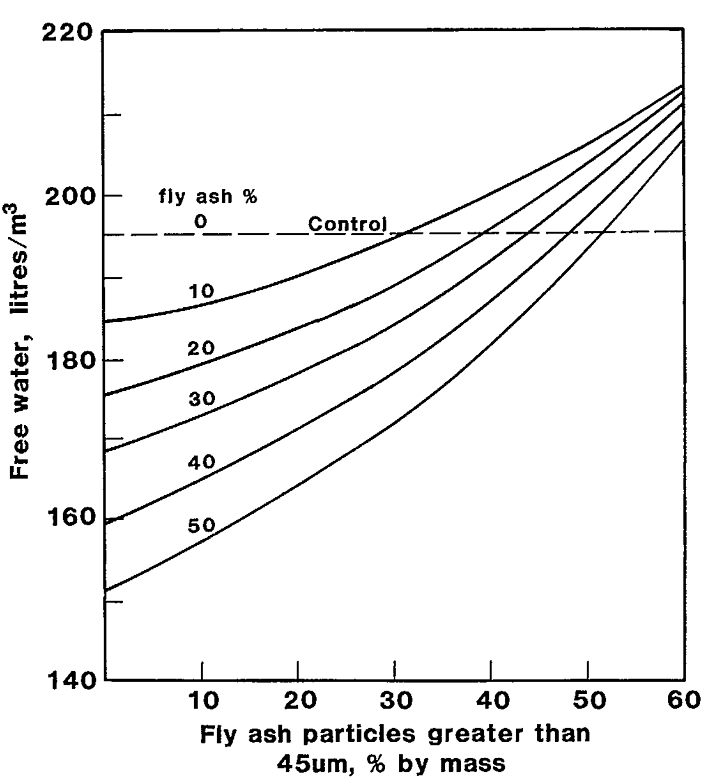

Fig. 3.2 — Influence of coarse particulate content of fly ash on the water required for equal workability in concrete (44)

Pasko and Larson (45) examined the amount of water required to maintain a nominal 63 mm slump in concrete mixes with partial replacement of cement by fly ash. They found that the water requirement was reduced by 7.2% in a mix in which 30% fly ash replaced 20% cement.

During investigations of the concrete materials for construction of the South Saskatchewan River Dam, Price (23) found that water requirement was not increased when additions of fly ash were made to concrete proportioned with fixed cement contents. The resulting concrete had a lower ratio of water to total cementitious material, while workability and cohesiveness of the mixes were improved.

Compton and MacInnis (46) reported that a concrete made by substituting 30% of the cement with an eastern Canadian fly ash required 7% less water than was required for a control concrete of equal slump.

Brown (47) examined the workability of four concretes of different water-to-cement ratios in which ash was substituted for cement on an equal volume basis. Slump, V-B time, and compacting factor were measured for each mix. It was found that both slump and V-B workability increased with increased ash substitution. The changes were found to depend upon the level of ash substitution (small additions sometimes being ineffectual) and on the water content. The data relating compacting factor and ash replacement are shown in Figure 3.3. An empirical estimate was made which indicates that for each 10% of ash substituted for cement, the compacting factor changed to the same degree as it would by increasing the water content of the mix by 3 to 4%.

In another series of experiments, Brown determined the effects of ash substitution for equal volumes of aggregate or sand in one concrete, keeping all other mix proportions (and the aggregate grading) constant. The test concrete was modified by replacing either 10, 20, or 40% of the volume of sand by ash, or 10, 20, or 40% of the volume of the total aggregate by ash. The replacement of 40% of the total aggregate gave a mix that was unworkable. The changes in slump and compacting factor are shown in Figure 3.4.

It was concluded from Brown's work that when ash was substituted for sand or total aggregate, workability increased to reach a maximum value at about 8% ash by volume of aggregate. Further substitution caused rapid decreases in workability.

In the cases of both aggregate and cement substitution, it was concluded that the observations were compatible with Hobbs' theoretical model (see below), if the ash was considered to be a part of the matrix and not a part of the aggregate.

The examples cited above are typical of many independent reports of improved plasticity and workability imparted by fly ash to concrete. Abdun-Nur (16), reviewing the subject, considered improved workability to be "almost axiomatic" when fly ash is used in properly adjusted concrete mixes. However, the literature does contain data to the contrary.

Brink and Halstead (48) reported that some fly ashes reduced the water requirement of test mortars, others (generally of higher carbon content) showed increased water requirement above that of control mortars. Welsh and Burton (49) reported loss of slump and flow for concretes made with some Australian fly ashes used to partially replace cement, when water content was maintained constant. Rehsi (50) reported that experience with a number of Indian fly ashes showed that all those examined increased the water requirement of concrete. In general, poor water demand characteristics have been found for fly ashes from older power plants where high carbon and coarse particle sizes are prevalent.

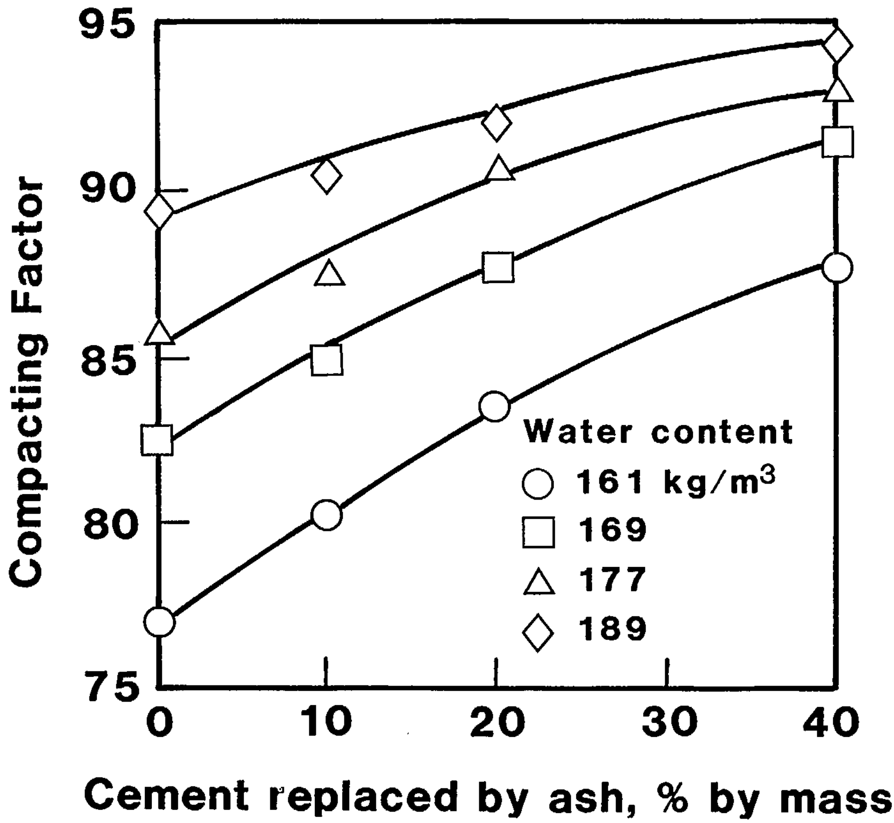

Fig. 3.3 — Influence of replacement of cement by fly ash on the workability of concrete (47)

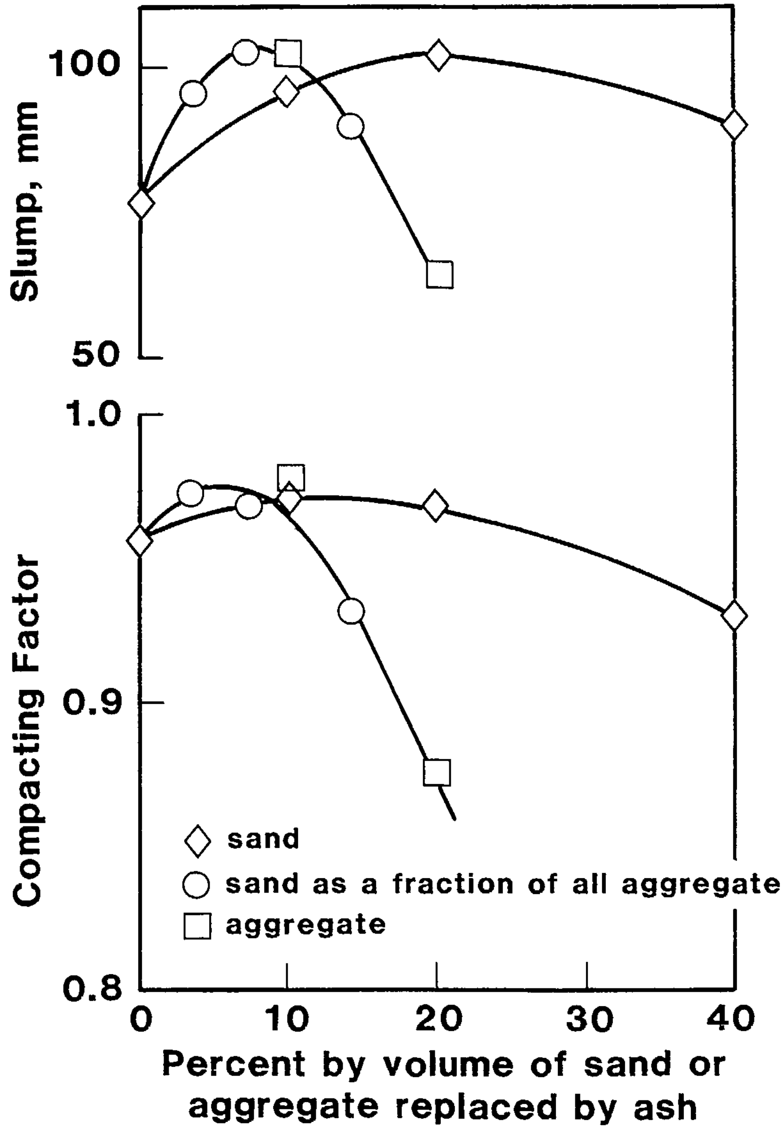

Fig. 3.4 — Influence of replacement of aggregate by fly ash on the workability of concrete (47)

Recent work at CANMET (38) has also shown that water reduction does not always accompany the inclusion of fly ash, even with ash of otherwise acceptable properties obtained from modern power plants. Of the 11 fly ash concretes for which data are presented in Table 3.2, 9 showed significant increases in slump at constant water content.

Because of the importance of workability to the proportioning of fly ash concretes, considerable effort has been made in recent years to develop a theoretical understanding of the rheology of fresh fly ash concrete.

In simple terms, the cement, water, fly ash, and fine sand particles, forming the paste in a mix, fill the void spaces between aggregate particles and, by coating them, provide cohesion and plasticity to the fluid mass.

Tattersall (51) has described the rheological behaviour of fresh concrete (at the low shear rates that are important in practice) in terms of a Bingham model* such that:

$$\tau - \tau_o = \mu_p \times \gamma$$

where:

τ = shear stress

γ = shear rate

τ_o = yield value

μ_p = coefficient of plastic viscosity.

Tattersall, and subsequently other co-workers, developed apparatus, described in detail by Tattersall and Banfill (52), to investigate the rheology of concrete based upon the Bingham model*.

In essence, the torque (T) and the rotational speed (N) of an impeller immersed in fresh concrete are measured at various speeds of rotation. A plot of T versus N, takes the form:

$$T = g + hN$$

which is exactly analogous to the Bingham expression; g and h correspond to the yield value and the plastic viscosity, respectively. The test has been termed the *two-point test* because properties are determined at a minimum of two shear rates, as compared to other standard tests where single-point (one shear rate) determinations are performed.

To understand the application of the test to fly ash concrete and the significance of the data so far obtained by this technique, some preliminary consideration of the observed behaviour of concrete under the test conditions is necessary. For a detailed treatment of the subject, the reader is referred to the original literature (52).

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*The Bingham Model of flow describes the relationship between shear stress (τ) and shear rate (γ) for a fluid which is non-Newtonian to the extent that, for shear to occur, a certain level of shear stress must be applied (called the yield stress). Once the yield stress is exceeded, further shear stress induces Newtonian behaviour, and shear strain becomes proportional to shear stress.

In general, the following observations have been made:

— g and h both decrease as the water-to-cement ratio increases.

— g increases as the fines content increases and the rate of increase is greater for richer mixes (or lower water-to-cement ratios).

— The effect of fines content on plastic viscosity (h) is more complex. For rich mixes, the value of h passes through a minimum that depends upon the water-to-cement and aggregate-to-cement ratios.

— Addition of water-reducing admixtures reduces yield stress and has an erratic effect on h.

— Superplasticizers markedly reduce g but show little effect on h.

— Air-entrainment reduces both g and h.

In terms of relationships between the *two-point* test and the slump test used in North America to measure workability, the following observation is made. Slump is measured at an effectively zero shear rate; thus it is seen to have an inverse relationship to the yield stress (g). Under circumstances where g is seen to decrease, an increased slump can be expected and would be interpreted in practice as an increased workability. Conversely, under circumstances in which increased workability (as determined by slump) is commonly reported, a decrease in yield stress may be anticipated.

To the present, data obtained by the two-point test for fly ash concrete are limited. Ellis (53) has reported measurements of g and h for fly ash concretes proportioned for mass and volume replacement of cement. The different densities of ash and cement result in an increased volume of total cementitious material when replacement is based on mass. Figure 3.5 shows the effect of replacement on medium workability concretes. Figure 3.6 shows the effect of replacement by mass on mixes of similar workability but with different cement contents and aggregate gradings. Both sets of data are taken to indicate that fly ash improves workability of concrete and, hence, reduces the water required for constant workability.

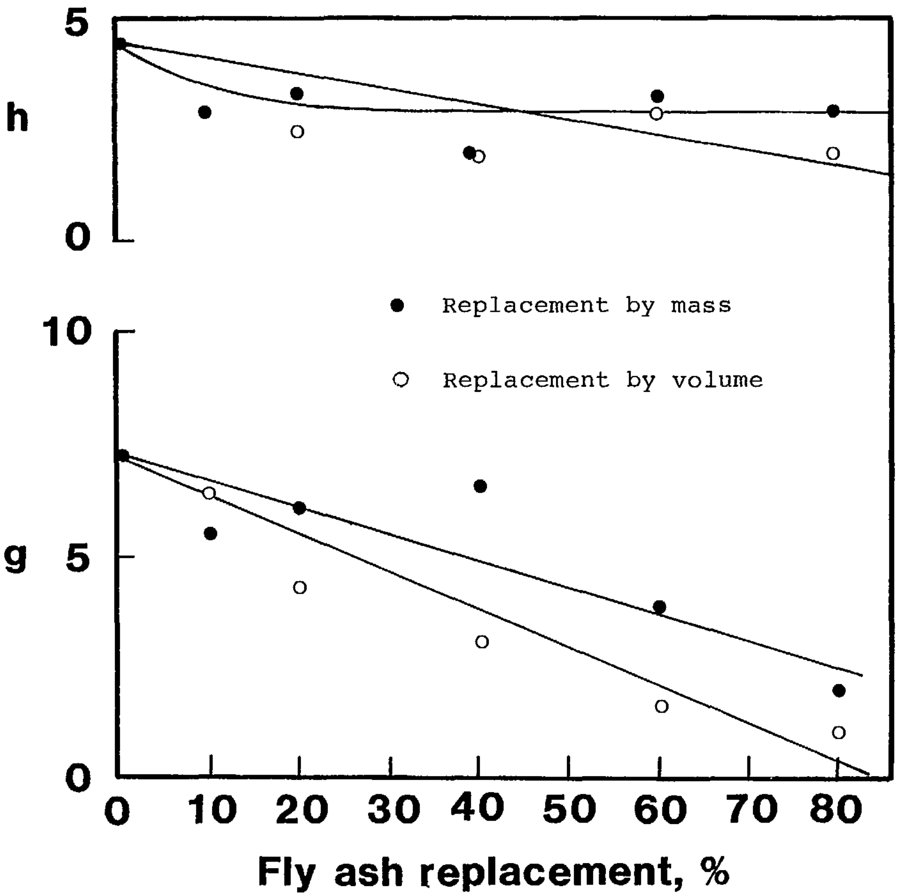

Fig. 3.5 — Influence of partial replacement of cement by fly ash on the yield stress and plastic viscosity of concrete (53)

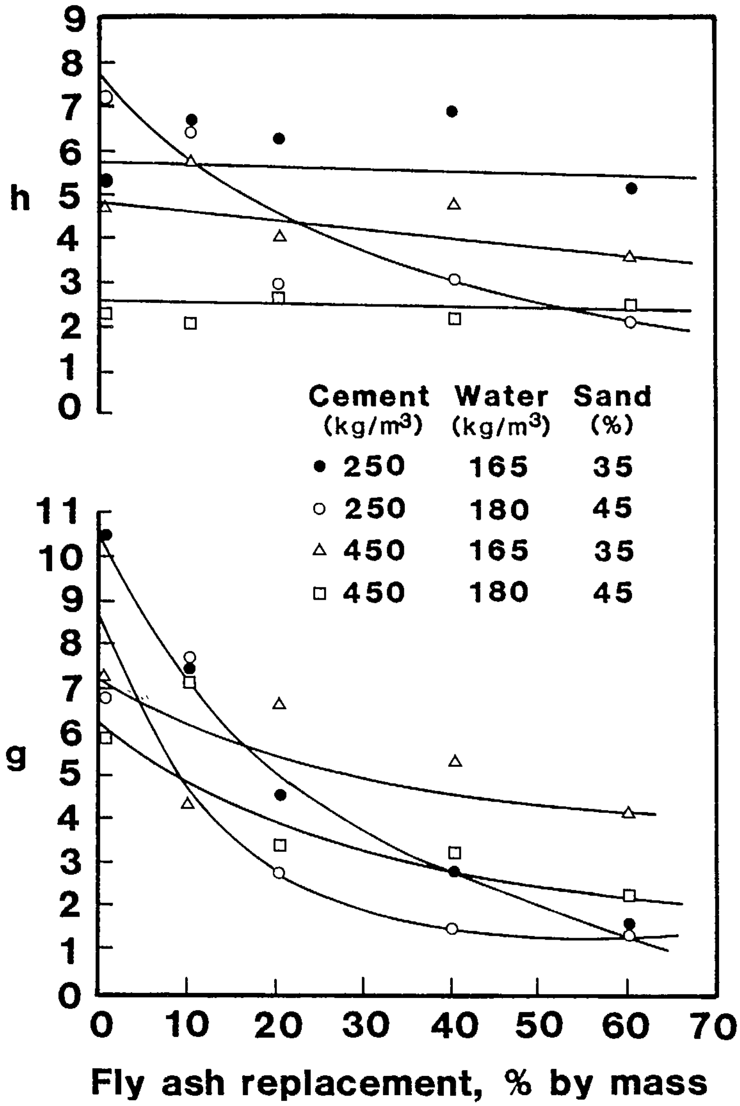

Fig. 3.6 — Influence of partial replacement of cement by fly ash on the yield stress and plastic viscosity of various concrete mixes (53)

Hobbs (54) has developed mathematical expressions relating the yield value and the plastic viscosity to volumetric parameters of concrete, and has shown these to be in agreement with viscosity data obtained by Ivanhov and Zacharieva (55) on fly ash–cement pastes and with workability measurements made by Brown (56) on concretes in which fly ash partially replaced cement.

For concrete in which the aggregate is replaced by fly ash, Hobbs' theory predicts that the yield value and the plastic viscosity decrease as the volume of fly ash increases, until minima are reached, and then increase as the aggregate replacement level is further increased. Hobbs concluded that the observed changes in slump, as the percentage of aggregate replaced by fly ash is increased, are in broad agreement with the changes in yield value and plastic viscosity for a Bingham suspension.

Ivanhov and Zacharieva (57), using vibro-viscometers, found similar effects produced by fly ash in concrete. They too established that fresh concrete can be approximated by the Bingham model and reported as follows:

— Yield stress and plastic viscosity were both found to be inversely related to the water-to-cement ratio, the extent of this relationship depending upon the surface area of the fly ash.

— Fine ash was found to be more effective at improving workability than coarse ash.

— Plastic viscosity was found to increase with an increase in the volume of paste at a constant ash to total cementitious ratio.

In essence then, these preliminary efforts to determine yield stress and plastic viscosity and to develop a theoretical base for understanding concrete rheology, indicate that fly ash can act to *plasticize* concrete.

Concrete using fly ash is generally reported to show reduced segregation and bleeding and to be more satisfactory than plain concrete when placed by pumping. An example of data relating to bleeding of fresh concrete is given in Figure 3.7.

Copeland (59) reported that in the field the use of fly ash was found to reduce bleeding in concretes made from aggregates known to produce harsh mixes normally prone to bleeding. Johnson (60) reported that most concrete made in the Cape Town (South Africa) area suffers from excessive bleeding due to a lack of fines in the locally available dune sands. He added that the problem can be overcome by increasing the overall paste volume by using fly ash in the concrete.

In the CANMET study (38), it was found (see Table 3.2) that all except 2 of the 11 ashes examined increased bleeding.

In line with the improved rheological properties, and as a result of the fine particulate content, some fly ashes give a very marked improvement in finish when used as a replacement for either sand or cement. Effects such as these make fly ash particularly valuable in lean mixes and in concretes made with aggregates deficient in fines.

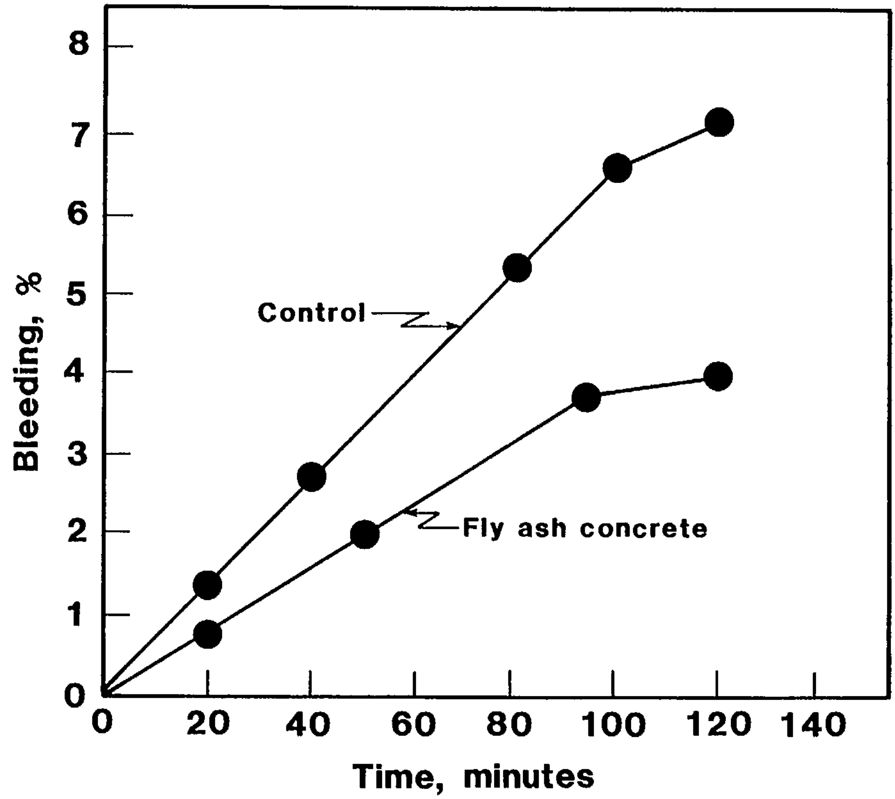

Fig. 3.7 — Relative bleeding of control and fly ash concretes (58)

Effect of Fly Ash on Temperature Rise of Fresh Concrete

The hydration or setting of portland cement paste is accompanied by an evolution of heat that causes a temperature rise in concrete. Replacement of cement by fly ash results in a reduction in the temperature rise in fresh concrete. This is of particular importance in mass concrete where cooling, following a large temperature rise, can lead to cracking. The first major use of fly ash in concrete was in the construction of a gravity dam where it was employed principally to control temperature rise (61).

Data reported by Elfert (62) show the effects of fly ash and a calcined diatomaceous shale on the temperature rise of mass concrete (Fig. 3.8).

Compton and MacInnis (46) reported the temperature-time curves shown in Figure 3.9 for two experimental concretes, one of which was made with a 30% substitution of an eastern Canadian fly ash for cement.

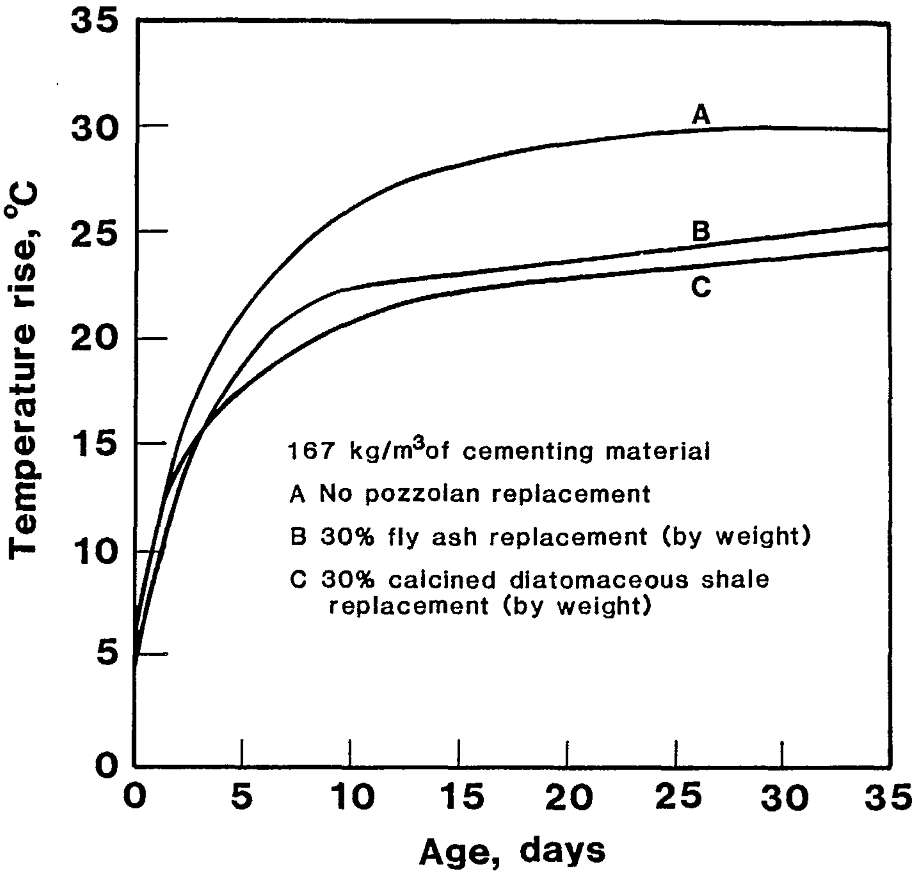

Fig. 3.8 — Influence of pozzolans on the temperature rise of concrete (62)

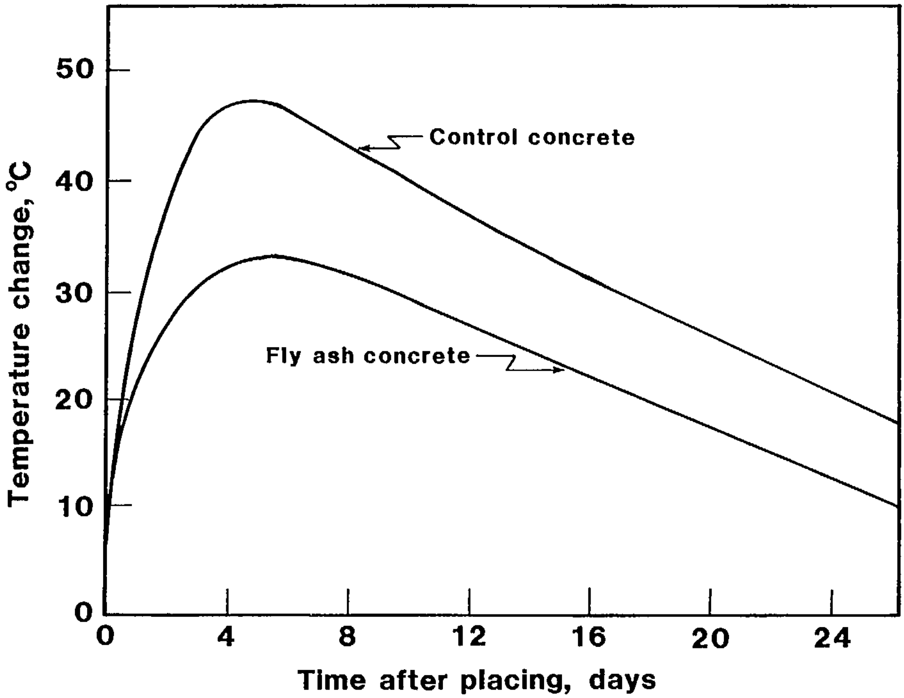

Fig. 3.9 — Temperature rise curves for fly ash and plain concrete test sections (46)

In modern construction, the use of mass concrete is no longer confined to structures such as dams. It is frequently used in foundations and structural members for many classes of buildings. The American Concrete Institute, Committee 116 (63), has defined mass concrete as:

> "... any volume of concrete with dimensions large enough to require that measures be taken to cope with generation of heat of hydration from the cement and attendant volume change to minimize cracking."

It has been estimated that the contribution of fly ash to early-age heat generation ranges from 15 to 30% of that of an equivalent mass of portland cement (36).

Temperature rise, of course, depends upon more factors than the rate of heat generation, including the rate of heat loss and the thermal properties of the concrete and its surroundings. Williams and Owens (64) have presented an estimation (Fig. 3.10) of the effect of element size on the temperature rise in fly ash concretes.

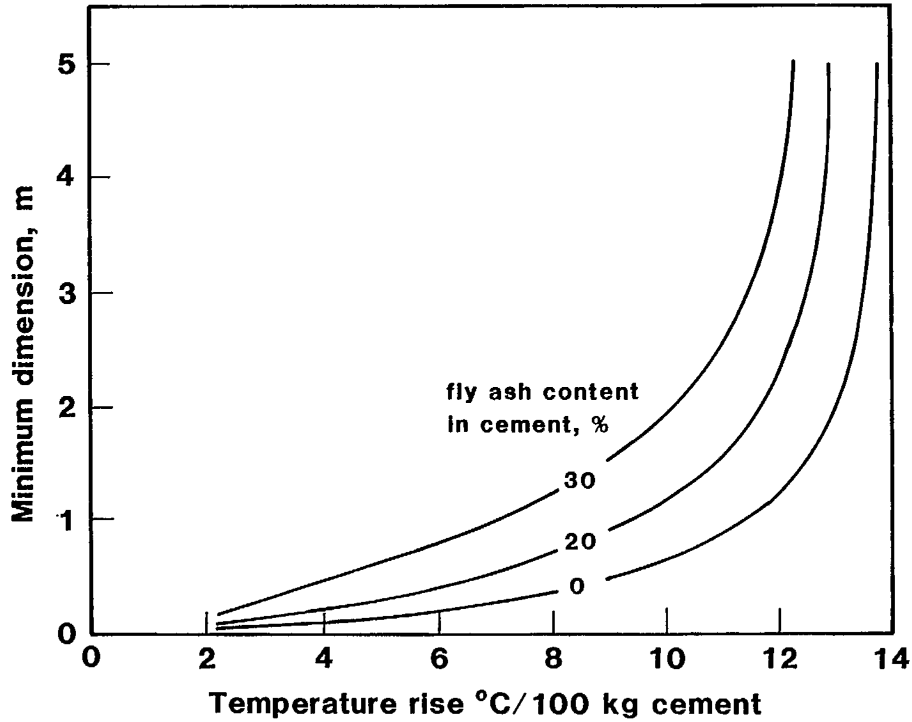

Fig. 3.10 — Effect of unit minimum size on the temperature rise in fly ash and plain concrete (64)

Bamforth (65) has reported on an extensive study of mass concrete containing fly ash or granulated blast-furnace slag as a substitute for cement. Included in this research was an in situ investigation of the temperature rise and the resulting strain in three large foundation units.

Three concretes were examined:

— a control mix with a portland cement content of 400 kg/m^3;

— a mix with 75% of the portland cement replaced by granulated slag;

— a mix with 30% of the portland cement replaced by a bituminous fly ash.

The concretes were placed in three foundation units each 4.5 m deep, the volumes ranging from 144 to 212 m^3. The units were instrumented to measure temperature changes and movement during the early stages of the heat-generation cycle. The measured temperature variation in each unit at mid-height is shown in Figure 3.11. Thermal gradients throughout each unit were also recorded, and the resulting observations are shown in Figure 3.12. As may be anticipated, the larger the quantity of cement replaced by fly ash or slag, the slower is the rate of temperature rise and the lower is the maximum temperature reached at any point in the concrete mass.

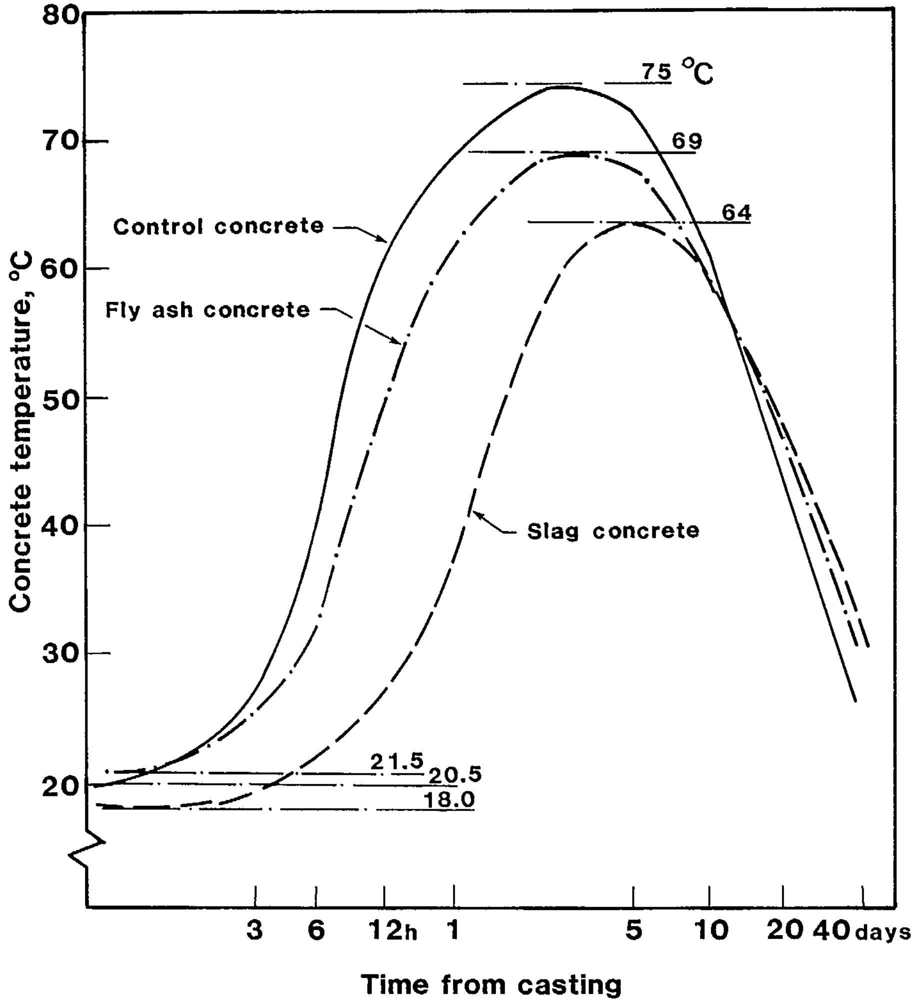

Fig. 3.11 — Variation of temperature recorded at mid-height in fly ash, slag, and plain concrete foundation units (65)

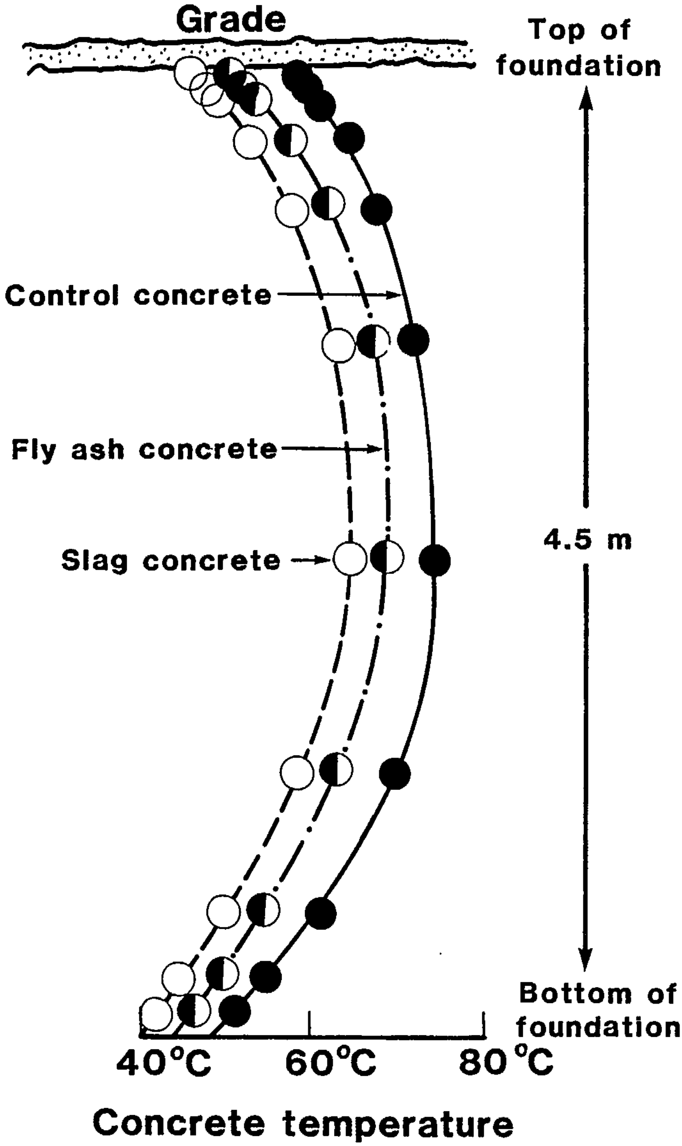

Fig. 3.12 — Vertical temperature distributions recorded at time of maximum temperature rise in fly ash, slag, and plain concrete foundation units (65)

Although it is probably reasonable to assume that all low-calcium fly ashes will reduce the rate of temperature rise when used as cement replacement, high-calcium fly ashes do not necessarily cause reduced heat evolution. In general, the rate of heat evolution parallels the rate of strength development (66). Some high-calcium ashes react very rapidly with water, thus generating excessive heat.

Crow and Dunstan (66) have reported the adiabatic temperature rise data on concrete mixes shown in Figure 3.13. Whereas concrete containing 25% of a low-calcium fly ash showed a reduced rate of heat generation, concrete with 25% of a high-calcium fly ash produced as much heat (at a similar rate) as a portland cement control.

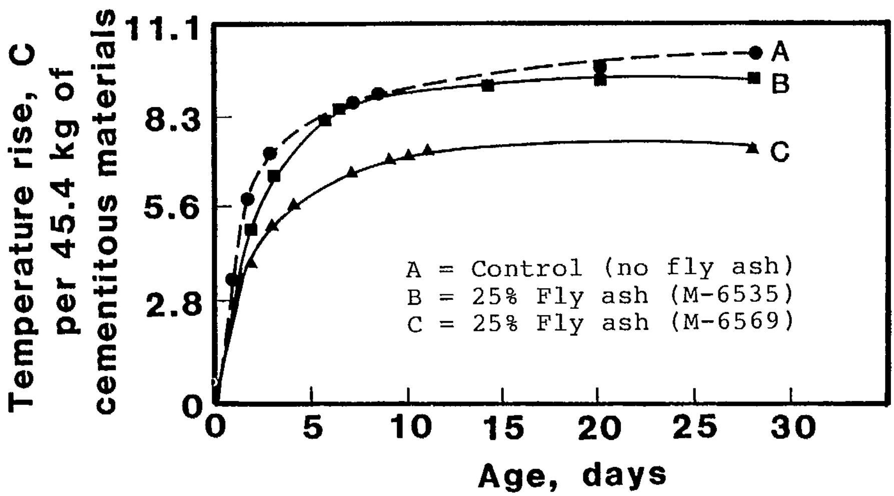

Fig. 3.13—Adiabatic temperature rise in concrete made with high-calcium fly ash (66)

Korac and Ukraincik (67) have reported the data shown in Figure 3.14 from in situ measurements of temperature rise for concrete containing high-calcium (22.93% CaO) fly ash from brown coal. The concrete made with cement containing 50% fly ash showed less temperature rise than the concrete with the commercially available cement containing 5% pozzolan and 15% slag.

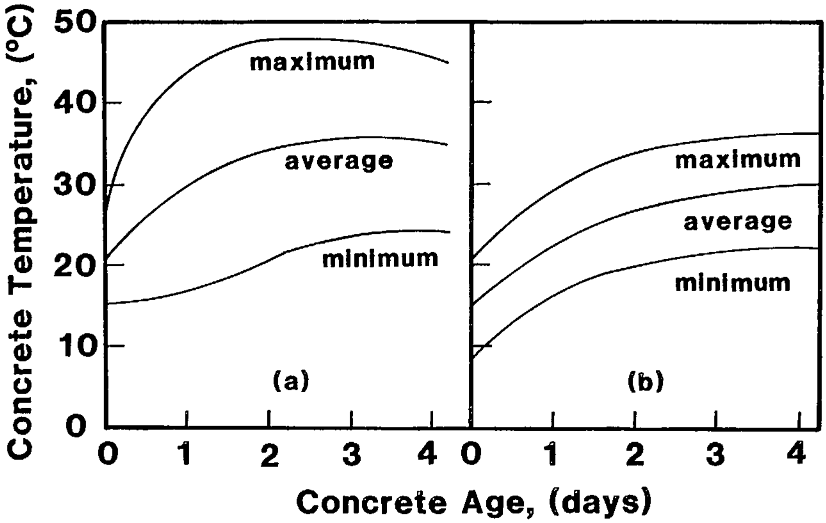

Fig. 3.14 — In situ temperature rise in concrete made with fly ash and two different cement types (67)

(a) = 5% pozzolan/15% slag-cement
(b) = 50% fly ash cement.

Effects of Fly Ash on Air-Entrainment in Fresh Concrete

Cycles of freezing and thawing are extremely destructive to water-saturated concretes that are not properly proportioned. Concrete will be frost-resistant if it is properly air-entrained, properly protected until some maturity has developed, and is made with sound coarse aggregate.

To obtain the desired number of correctly spaced air voids in hardened concrete that are necessary for frost resistance, an air-entraining admixture (AEA) is added in a prescribed dosage to the concrete during mixing. Two attributes are important: the AEA must produce the required volume of air bubbles of the desired size and spacing in the concrete; it must do so in a manner that allows the air content to remain as a stable dispersion while the concrete is mixed, transported, and placed.

It has been reported that the use of some fly ashes causes an increase in the quantity of air-entraining agent required to produce a given level of air-entrainment in fresh concrete (45,68-70).

Larson (69), presenting work on the use of fly ash in air-entrained concrete and reviewing the work of other investigators (70-74), concluded that the primary effect of fly ash was upon AEA demand, rather than upon air-entrainment as such.

In a study of six Type IP cements, Perenchio and Klieger (75) found that AEA requirements were higher in every case for the Type IP cements than for comparable Type I cements. Increases ranged from 15 to 210%. AEA demand in fly ash concrete was generally ascribed to the adsorption of air-entraining agents by carbon in the fly ash. A similarly wide range of AEA demand was found in the CANMET study (see Table 3.2) with most of the fly ashes examined.

The problem of air-entrainment of fly ash concretes has been the most frequently quoted factor impeding their widespread acceptance in construction in Canada. Recent research has fostered some better understanding of this problem.

Consideration of air-entrainment requires examination of three properties:

— air content

— stability of air content

— air-void parameters in the hardened concrete.

Air content and the stability of air content are discussed in this chapter in relation to fresh concrete. The parameters of air-void systems and other issues related to the freezing and thawing resistance of hardened concrete are considered in Chapter 7.

Gebler and Klieger (76) have examined ten different fly ashes representing a range of chemical and physical properties. Carbon content ranged from 0.14 to 4.19%, total organics ranged from 0.09 to 1.04%, CaO ranged from 1.20 to 29.00%, and fineness (as % retained on a 45 μm sieve) ranged from 11.24 to 38.45%.

Concretes were proportioned by simple replacement of 25% of the cement by fly ash (by mass). All mixes were proportioned to have 75 ± 25 mm slump and 6 ± 1% air. The only air-entraining admixture used was neutralized Vinsol resin.

The AEA demand of the control concrete (for 6% air content) showed the following results:

— For ashes containing more than 10% CaO, the range of AEA demand was 126 to 173%.

— For ashes containing less than 10% CaO, the range of AEA demand was 170 to 553%.

Regression analyses were made to test for correlation between AEA demand and a number of chemical and physical parameters. The authors reported the following variables to be significantly related to AEA demand:

— total organic matter ($R_c = 0.96$);

— carbon content (also related to loss on ignition), ($R_c = 0.75$).

The air contents remaining after completion of initial mixing for periods up to 90 minutes were determined, and the data shown in Table 3.4 were reported. Analysis of the data indicated a correlation between AEA demand and air retained in fresh concrete (R_c = 0.81). As air-entraining agent dosage increased, concretes containing fly ash tended to show instability of air content in the fresh state.

Table 3.4 — Air-entraining admixture demand and stability of entrained air in fly ash concretes*

Ident.	Class	AEA demand (mL/kg of cementitious material)	Per cent air contained** Time after mixing (minutes) 30	60	90
A	C	5.53	83	83	80
B	F	9.13	77	64	58
C	F	24.14	67	54	41
D	F	10.43	82	64	62
E	F	8.29	82	77	68
F	C	7.56	96	93	94
G	C	6.92	87	82	76
H	F	7.43	91	86	87
I	C	6.53	98	98	103
J	F	18.98	76	69	61
Control Mixes					
307 kg/m³		4.37	91	85	80
281 kg/m³		3.81	88	85	81

*From reference 76.
**Expressed as percentage of initial air content.

Gebler and Klieger offered the following summary of the findings and conclusions relevant to air-entrainment in fresh concrete:

> "Generally, concretes containing Class C fly ash require less air-entraining admixture than those concretes with Class F fly ash. All concretes with fly ash required more air-entraining admixture than the portland-cement concretes without fly ash.
>
> "Plastic concrete containing Class C fly ash tended to lose less air than concretes with Class F ash.
>
> "As the air-entraining admixture requirement increases for a concrete containing fly ash, the air loss increases.
>
> "Air contents in plastic concrete containing Class F fly ash were reduced as much as 59%, 90 minutes after completion of mixing.

"As the organic matter content, carbon content and loss-on-ignition of fly ash increase, the air-entraining admixture requirement increases as does the loss of air in plastic concrete.

"Generally, as total alkalis in fly ash increase, the air-entraining admixture requirement decreases.

"As the specific gravity of a fly ash increases, the retention of air in concrete increases. Concrete containing a fly ash that has a high lime content (Class C fly ash) and less organic matter tends to be less vulnerable to loss of air.

"Generally, as the SO_3 content of fly ash increases, the retained air in concrete increases."

Fly ash is not alone in causing increased AEA demand in fresh concrete. Other mineral by-products behave in a similar manner, and some portland cements have been found to require excessive additions of air-entraining admixtures (77-81). Virtanen (81) has reported the comparative data on AEA demand shown in Figure 3.15.

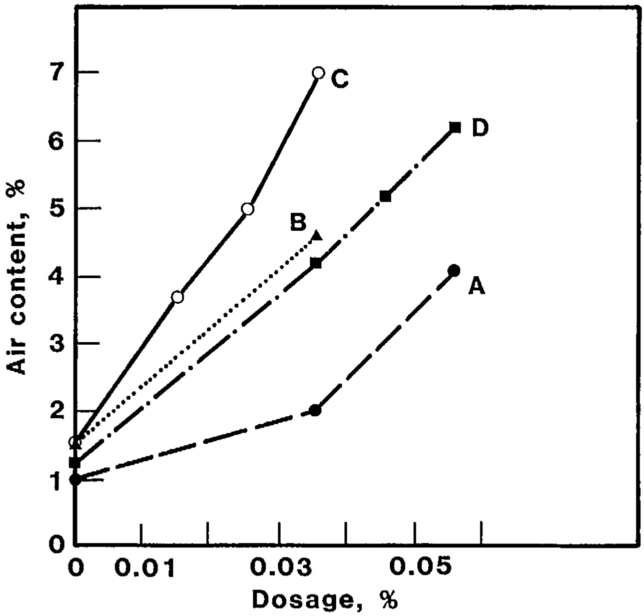

Fig. 3.15 — Air content of fresh concrete as a function of dosage of air-entraining agent (81)

Key: A = Concretes incorporating ground granulated blast furnace slag
B = Concretes incorporating condensed silica fume
C = Control concretes
D = Concretes incorporating fly ash.

Burns et al. (82) have reported that pre-exposure of fly ash containing carbon to chlorine gas, calcium hypochlorite, or some surfactants effectively reduced the demand for air-entraining admixture in concrete. This was interpreted as being evidence of the active nature of the carbon in fly ash and its deactivation by the adsorption of chemically reactive species that did not themselves interfere with air-entrainment.

To date, no adequate theory has been developed to explain the various observations related to the interference that is sometimes observed between fly ash and air-entraining agents. Clearly, research is needed into the mechanisms of air-entrainment of concrete and into the ways that supplementary cementing materials influence the behaviour of air-entraining admixtures.

4. EFFECTS OF FLY ASH ON THE STRUCTURAL PROPERTIES OF HARDENED CONCRETE

"Strength is not the only important property of concrete but it is a vital property, regardless of the strength level required. Suitable strength can be obtained with a wide range of mix ingredients, provided we understand their role and influence. Fly ash is no exception: use of suitable fly ash can lead to high strength at the desired age." — Adam M. Neville, 1984.

Fly ash affects most of the properties of hardened concrete in one way or another. This chapter is concerned with the ways in which the use of fly ash influences the following properties:

— strength development

— elasticity

— creep, shrinkage, and thermal expansion.

A recent CANMET study (38) has shown that concretes made under similar conditions, from the same cement and aggregates, but incorporating different fly ashes, may develop strength at markedly different rates. Table 4.1 shows the strength development up to 91 days of the concrete mixes presented in Table 3.1 (Chapter 3); the different reactivities of the fly ashes are clearly seen from these data.

Strength Development in Fly Ash Concrete

As discussed in Chapter 2, the main factors determining strength in concrete are the amount of cement used and the water-to-cement ratio. In practice, these are established as a compromise between the needs of workability in the freshly mixed state, strength and durability in the hardened state, and cost. The degree and manner in which fly ash affects workability is a major factor in its influence on strength development. As was shown in Chapter 3, a fly ash that permits the total water requirement to be reduced in concrete will generally present no problems with regard to the selection of mix proportions permitting any desired rate of strength development.

This chapter is concerned with the factors, other than mix proportioning and workability, that determine the rate of strength development in fly ash concrete. In essence, these are the fundamental characteristics of fly ash that mix proportioning seeks to accommodate in practice.

Table 4.1 — Properties of hardened concrete*

Mixture No **	Compressive strength of 150 × 300-mm cylinders, MPa				Flexural strength of 75 × 100 × 400-mm prisms, MPa		
	7 days	28 days	91 days	365 days	14 days	28 days	91 days
Control	23.4	30.6	34.9	39.2	4.9	5.4	5.9
F1	18.4	25.7	31.4	38.3	4.4	4.4	5.4
F2	16.9	25.2	34.8	37.0	3.9	4.8	5.5
F3	14.4	21.0	27.6	34.4	4.0	5.0	5.3
F4	17.8	23.3	32.3	36.9	4.1	4.4	5.2
F5	20.1	28.0	33.9	44.3	3.5	4.4	5.3
F6	18.4	24.8	31.8	39.2	3.5	4.6	5.6
F7	16.7	24.1	29.1	35.7	3.9	4.5	5.4
F8	17.9	27.7	29.0	40.4	4.6	5.0	6.1
F9	16.7	24.9	31.1	35.6	4.3	4.2	5.7
F10	19.2	28.5	33.7	39.7	4.1	5.1	5.8
F11	21.1	29.4	35.3	40.1	4.8	5.3	6.6

*From reference 38.
**See Tables 3.1 and 3.2 for fly ash and mix proportion data.

Many variables influence the strength development of fly ash concrete, the most important being the following:

- — the properties of the fly ash
- — chemical composition
- — particle size
- — reactivity
- — the temperature and other curing conditions.

Effect of fly ash type on concrete strength

The first difference between fly ashes that should be recognized is that some are cementitious even in the absence of portland cement. Frequently, these are the so-called Class C or high-calcium fly ashes usually produced at power plants burning subbituminous or lignitic coals.

In general, the rate of strength development in concretes tends to be only marginally affected by high-calcium fly ashes. A number of authors have noted that concrete incorporating high-calcium fly ashes can be made on an equal weight or equal volume replacement basis without any significant effect on strength at early ages (83,84).

Yuan and Cook (83) have examined the strength development of concretes with and without high-calcium fly ash (CaO = 30.3%). The data from their research are shown in Figure 4.1. Using a simple replacement method of mix proportioning (Table 4.2) they found the rate of strength development of fly ash concrete to be comparable to that of the control concrete, with or without air-entrainment.

Table 4.2 — Mix designations, proportions, and properties of concretes incorporating high-calcium fly ash*

Mix designation	C1	C2	C3	C4
Proportions		kg/m^3		
Cement	387	309	272	196
Fly ash	0	77	117	196
Cement + fly ash	387	386	389	392
Water	145	145	146	147
Coarse aggregate	1146	1144	1153	1160
Fine aggregate	701	690	678	654
Properties				
Slump (cm)	3	9	12	21
Air content (%)	2.1	1.9	1.9	1.4
Unit weight (kg/m^3)	2377	2364	2364	2352
Fly ash as per cent of cement	0	20	30	50

*From reference 83.

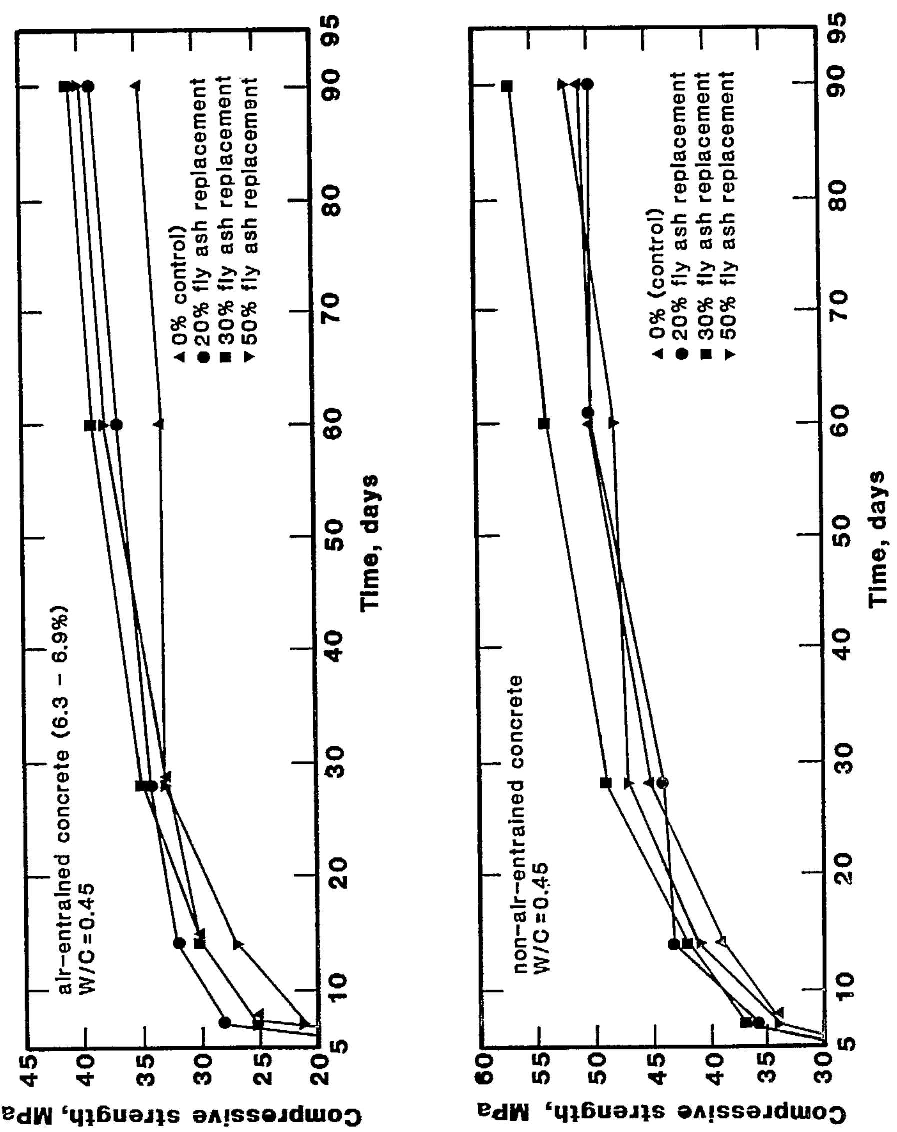

Fig. 4.1 — Compressive strength development of concretes containing high-calcium fly ash (83)

Raba and Smith (84) examined the concrete-making properties of a sub-bituminous fly ash (CaO = 20.0%). Data on compressive strength gain attributed to the presence of high-calcium fly ash are shown in Table 4.3. It should be noted that the mix proportioning approach used comprised replacement of fine aggregate by volume, the mass of cement and coarse aggregate being kept constant for each series of determinations.

Table 4.3 — Compressive strength gains attributed to the presence of high-calcium fly ash*

Cement	Fly ash	Compressive Strength**		
		Per cent of Control		Per cent Gained
kg/m³		28 days	56 days	From 28 to 56 days
91	50	318	354	15.2
	59	352	393	16.0
	68	401	435	13.6
	77	471	494	10.5
136	50	210	228	10.2
	59	231	256	11.8
	68	245	269	11.1
	77	253	274	10.3
182	50	149	155	8.2
	59	153	167	12.4
	68	163	177	12.0
	77	187	190	6.2

*From reference 84.
**Note: In these mixes, fly ash was used to replace fine aggregate.

Low-calcium fly ashes, the so-called Class F ashes, usually formed from bituminous coals, were the first to be examined for use in concrete, and much that has been written on the behaviour of fly ash concrete has been determined by examination of materials using Class F ashes. In addition, the ashes used in much of the early work came from older power plants and were coarse in particle size, contained unburned fuel, and were often relatively inactive as pozzolans. Used in concrete, proportioned by simple replacement, these ashes showed exceptionally slow rates of strength development. Such observations have led to the development of generalized opinions that "fly ash reduces strength at all ages" (85). Conversely, they have resulted in considerable efforts to understand the factors affecting strength in fly ash concrete and the ways in which to manipulate them in order to obtain desired rates of strength gain.

Particle size and strength of fly ash concretes

Particle size can influence strength development in two ways. First, as discussed in Chapter 3, particles larger than 45 μm appear to influence water requirement in an adverse way. Thus, they act counter to the needs of the proportioning methods used to compensate for the slow rate of reaction of fly ash at early ages. Second, cementing activity occurs on the surface of solid phases, through heterogeneous processes involving the diffusion and dissolution of materials in concentrated pastes. Surface area must play a considerable role in determining the kinetics of such processes.

Direct experimental evidence of the influence of particle size on strength development is contradictory.

In a study of 36 concrete mixes, most containing fly ashes of a wide variety of properties, Crow and Dunstan (66) concluded that:

> "...fineness of ash compared loosely with the pozzolanic activity, thus finer ashes reacted more readily with portland cement. Fineness appeared more critical to the reaction of the low-calcium ashes than to those higher in calcium content."

Wesche and vom Berg (86), on the other hand, found no correlation between fineness and compressive strength of mortars at 7 or 28 days and a minor correlation at 90 days from more than 340 tests on fly ashes from 14 sources.

In some respects, these results are to be expected when samples from a large number of sources are examined in experiments designed to determine only one factor. Many fly ash-related variables influence strength development; poor correlation with particle size only indicates that particle size is not *the dominant variable* in fly ash reactivity. To establish a relationship to particle size, it is necessary either to limit all other variables to a minimum number or to perform a multi-variable experiment. To date, only the former approach has been taken.

Both Joshi (87) and Ravina (88) have exploited the phenomenon of particle size segregation that occurs in electrostatic precipitators, to obtain fly ash fractions of different fineness from a single source.

When fly ash is collected in a multi-stage, electrostatic precipitator, segregation by particle size occurs; particles in the finer size categories are collected in the chambers furthest from the furnace. By taking ash from each chamber, particles of different size distributions from the same source are obtained at the same time.

Unfortunately, size is not the only factor that differs between the chambers. The chemical properties, density, and morphology of the particles also differ. Chemically, carbon tends to be segregated with the larger particles, and alkali sulphates and chlorides tend to be collected on the surface of the finer particles in the cooler regions of the precipitator. Low-density particles are differentially distributed in the precipitator; cenospheres and irregularly shaped particles tend to precipitate from the gases in the first chamber and, thus, affect average density measurements. However, examination of ashes from one source, segregated by size, would seem to be the simplest way of determining the influence of particle size on strength, given the limitation that the results may be weighted by other, uncontrolled factors.

Joshi (87) examined ash from different chambers of the precipitator of a modern power plant (Sundance, Alberta) burning subbituminous coal. The ashes were found to have the following contents of particles larger than 45 μm:

Ash	% retained on a 45 μm sieve
1	5
2	16
3	32
4	38

Concretes were made with 10 and 20% replacement of cement for each of the four ashes. Resulting compressive strength data are shown in Figure 4.2.

It is clear from these experiments that at both 10 and 20% replacement the finer fly ashes imparted greater strength. The coarse fraction appears not to have contributed significantly to the strength.

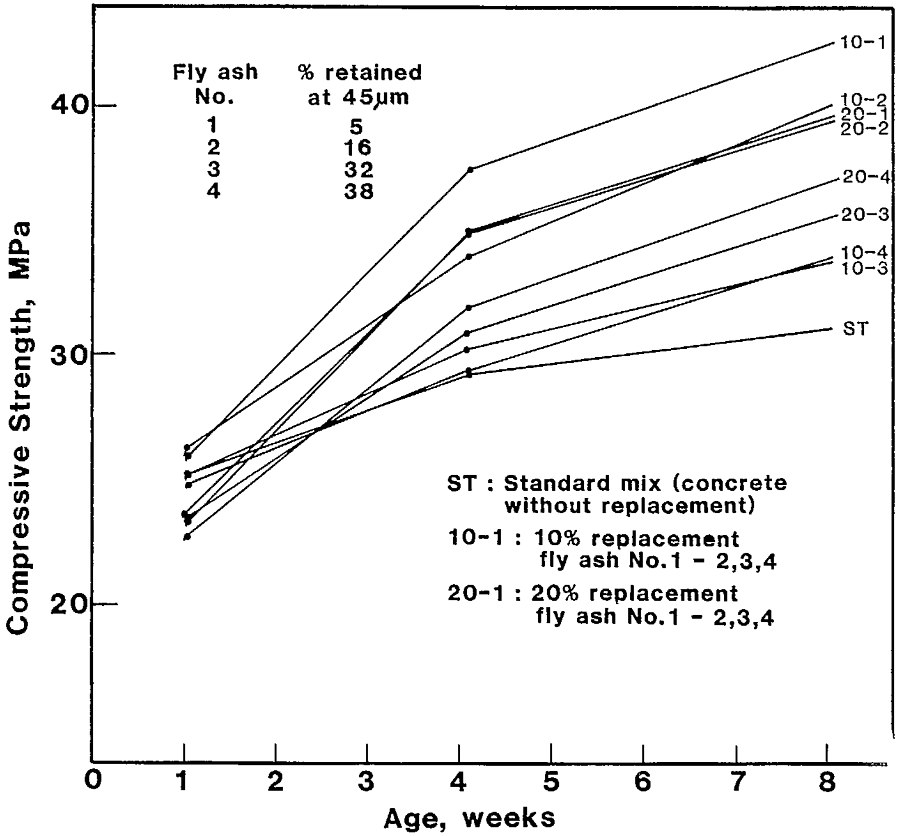

Fig. 4.2 — Effect of coarse fractions of fly ash on compressive strength development of concretes (87)

Ravina (88) reported similar results from an examination of the pozzolanic index of low-calcium ash from each of four hoppers (chambers) from one source.

An alternative way to obtain sized ash from one source is by grinding. Monk (89) has examined ashes from four base-load power plants as blended cements and as interground cements with portland cement. The principal conclusions from his research were:

- Portland-fly ash cements prepared by intergrinding clinker, gypsum, and fly ash have a water demand equal to, or lower than, that of equivalent cements produced by blending ordinary portland cement and fly ash.
- Intergrinding did not negate the workability benefit of fly ash. Breakdown of spherical particles was not observed, but the agglomerates of spheres in coarse ashes were separated.
- Compressive strengths at all ages for the interground cements were equal to, or higher than, those for the blended cements.
- Intergrinding resulted in an improvement of coarse ashes, with respect to water-reducing properties, and also pozzolanic activity, as indicated by compressive strength improvement at later ages.

It would appear that when experimental efforts are made to eliminate the effects of multi-variable interference, there is a well-defined correlation between strength development and particle size (or surface area). This suggests that for ash from one source, particle size is an important indication of reactivity. This viewpoint is reflected in almost all quality-control procedures that have been recommended for selecting ash for use in concrete and has been incorporated in most Standards (see Chapter 8).

Fly ash reactivity

Pozzolanic activity, although well established as a phenomenon, is far from being well understood. Much of the research currently in progress on fly ash is directed to understanding pozzolanic reactions. It is not within the scope of this report to discuss this work in any detail, and the reader is referred to other published sources (19,90-93) for review material on this subject.

However, some aspects of pozzolanic reactivity are of immediate relevance to the behaviour of fly ash concrete in the hardened state. In particular, the effects of temperature during curing on the subsequent strength of concrete are of great practical importance and, as will be discussed, appear to be closely related to the fundamental nature of pozzolanic action.

Temperature and the development of strength in fly ash concretes

When concrete made with portland cement is cured at temperatures in excess of 30°C, an increase is seen in strength at early ages but a marked decrease in strength is noted in the mature concrete (94).

Concrete containing fly ash behaves significantly differently. Figure 4.3 shows the general way in which the temperature, reached during early ages of curing, influences the 28-day strength of concrete. In contrast to the loss of strength that occurs with ordinary portland cement, fly ash concretes show strength gains as a consequence of heating. This is of great value in the construction of mass concrete or in concrete construction at elevated temperatures.

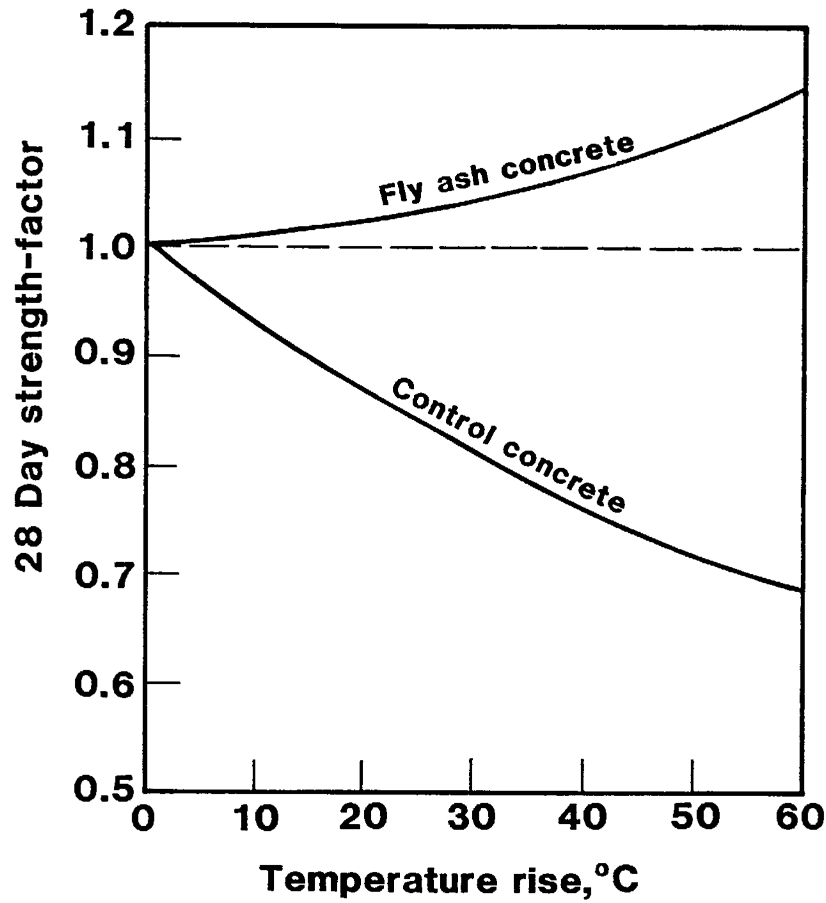

Fig. 4.3 — Effect of temperature rise during curing on the compressive strength development of concretes (64)

Kobayashi (95) reported that fly ash was used at a 25% cement replacement level in the concrete for an intake tunnel of the Kurobegwa No. 3 Power Station in Japan (96). Because this tunnel is located in rock at temperatures of 100 to 160°C, fly ash was used as a means to combat the loss of strength that would have resulted had portland cement concrete been used alone.

Bamforth (65) has reported on the in situ and laboratory-observed effects of temperature on the strength development of mass concrete containing fly ash or slag substituents.

Figure 4.4a shows the strength development of standard cubes made from the three concretes studied by Bamforth (see Chapter 3) under standard laboratory curing conditions. Approximate strength equality was reached at 28 days and, in fact, the strength of the fly ash concrete was close to equality with the control concrete at earlier ages.

Figure 4.4b shows the effects of curing under *temperature-matched* conditions, where the effects of the early age temperature cycle at the centre of the concrete mass were simulated. In all cases, early strength development was accelerated. However, at 28 days, whereas the strength of the fly ash concrete was enhanced by temperature, the strength of the control concrete was significantly less, being 30% below that of the standard water-cured concrete.

Ravina (97) has discussed how the effects of fly ash in concrete cured at moderately elevated temperatures can be used to advantage in precast operations. Ravina's paper is of considerable interest also with regard to the way in which fly ash was found to react in concrete cured under a controlled regime that included some exposure to heat.

Ravina examined concrete made with fly ash from the same source but of two size fractions:

— coarse ash from the first precipitator field with 30 to 35% retained on a 45-μm sieve;

— fine ash from the third precipitator field with 14 to 17% retained on a 45-μm sieve.

The following curing regime was used:

— Control specimens were kept for 22 hours at 23°C prior to demolding, and then placed for 7 days in the fog-room at 23°C. They were then stored at 23°C and 65% RH until being tested.

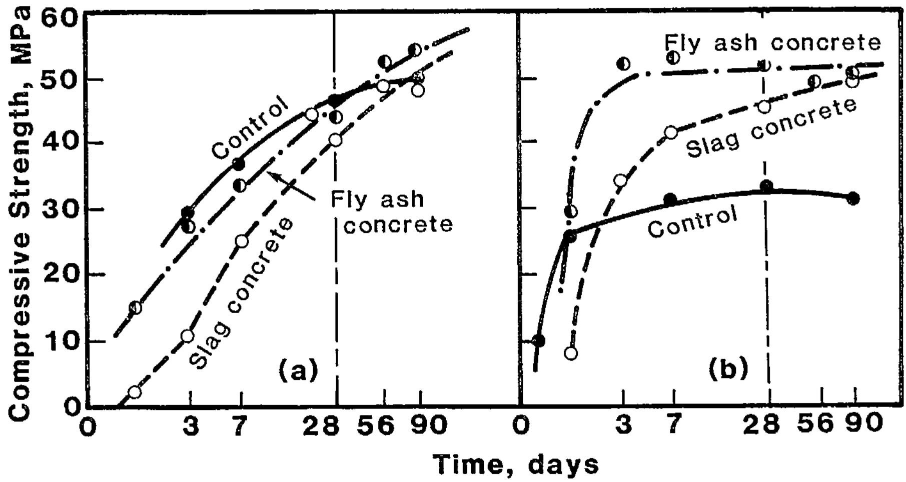

Fig. 4.4 — Compressive strength development of concretes: (a) cured under normal conditions; (b) cured by temperature matching (65)

Thermally cured specimens were kept at 23°C for two hours and then transferred to a steam chamber where the temperature was raised from 23 to 75°C over a two-hour period and kept at 75°C for four hours. Heating was then discontinued and the specimens were allowed to cool in the chamber. After 22 hours the samples were demolded and then stored in the same conditions as the control specimens.

Two series of non-air-entrained mixes were made (Table 4.4). In the first series, only coarse ash was used, replacing all or 50% by volume of the pit sand. In the second series, fine fly ash was used to replace 20% of the cement (by weight), and coarse ash replaced 50% (by volume) of the sand. Control mixes containing no fly ash, at two cement content levels, were also examined.

Table 4.4 — Mix designations and proportions of concretes cured at elevated temperatures*

Mix designation	I-A	I-B	I-C	II-A	II-B	III
Proportions	kg/m³					
Coarse and Medium aggregate	1165	1165	1125	1165	1165	1160
Quarry sand	535	535	520	535	535	535
Pit sand	380	190	—	370	180	430
Cement	300	300	300	240	240	240
Water	205	210	230	190	200	205
Coarse fly ash	—	155	305	—	150	—
Fine fly ash	—	—	—	60	60	—

*From reference 97.

The compressive strength data from this study are shown in Figure 4.5, from which the author drew the following conclusions:

- Large quantities of fly ash may be used effectively in concrete cured at elevated temperatures, with a significant improvement in its compressive strength, in contrast to the rather limited contribution under normal curing conditions at ages up to 28 days.
- The beneficial effect of curing at elevated temperatures, on coarse and fine fly ash concrete, is significant at an early age and continues to later ages.

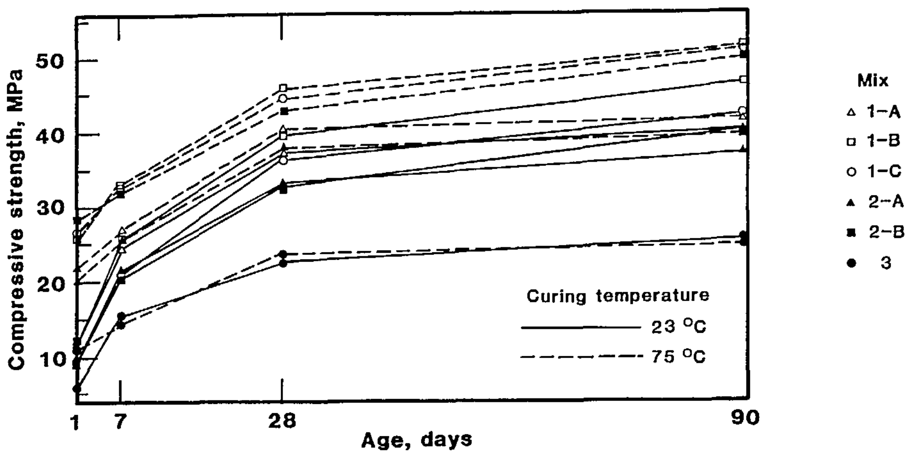

Fig. 4.5 — Effect of temperature during curing on the compressive strength development of concretes incorporating fine and coarse fractions of fly ash (97) (Note: For mix details see Table 4.4.)

Ravina's work and the observations of other authors (4,64) raise some significant issues with regard to the nature of pozzolanic reactivity. The following would seem to warrant further investigation:

- The rate of reaction of fly ash-cement systems is clearly increased by temperature, as is the case for portland cement. Yet the products of hydration do not exhibit the poor mechanical properties associated with curing portland cement at elevated temperatures. This would suggest that the products of fly ash-cement hydration, their relative proportions or their morphology, are significantly different from those formed from thermally accelerated hydration of portland cement alone.

- The rate of reaction of fly ash in cement systems is so significantly increased by temperature, that the effects of particle size on pozzolanic behaviour are largely overcome. This suggests that some pozzolanic activity tests that use thermal acceleration may give seriously misleading results.
- The pozzolanic reaction, once initiated by heat, appears to continue when the source of external heating is removed, even with coarse fly ash. This indicates the possible existence of an activation effect, similar to that observed for slags, that has not previously been associated with pozzolanic activity.

The sensitivity of fly ash to elevated temperature implies that it will also be sensitive to reduced temperature with a consequent reduction in the rate of strength development. This has been observed in practice and it is generally noted that fly ash concretes require more attention to curing in cold weather.

Effect of Fly Ash on Elastic Properties of Concrete

Published data indicate that fly ash has little influence on the elastic properties of concrete.

Abdun-Nur (16) makes the following observations on the early literature citations.

> "The modulus of elasticity of fly ash concrete is lower at early ages, and higher at later ages (2,98). In general, fly ash increases the modulus of elasticity of concrete when concretes of the same strength with and without fly ash are compared (99-101)."

Lane and Best (40) state as follows:

> "Fly ash properties controlling the compressive strength of concrete also influence the modulus of elasticity but to a lower extent. The modulus of elasticity, like compressive strength, is lower at early strength and higher at ultimate strength when compared with concrete without fly ash."

Figure 4.6 shows typical stress–strain relationships for concrete with and without fly ash.

Crow and Dunstan (66), reporting on an examination of the properties of 36 concretes, most containing fly ash at different levels and from different sources, concluded as follows with regard to elastic properties:

"The elastic properties of concretes containing both portland cement and fly ash are similar to those expected with portland cement (alone). The modulus of elasticity and Poisson's ratio both increased with age, paralleling the compressive strength development. The modulus of elasticity ranged from a low at 28 days of 18.8 GPa to a high of 39.6 GPa at 365 days. Most of the ashes (in concrete) had a 28 day Poisson's ratio in the range of 0.14 to 0.25."

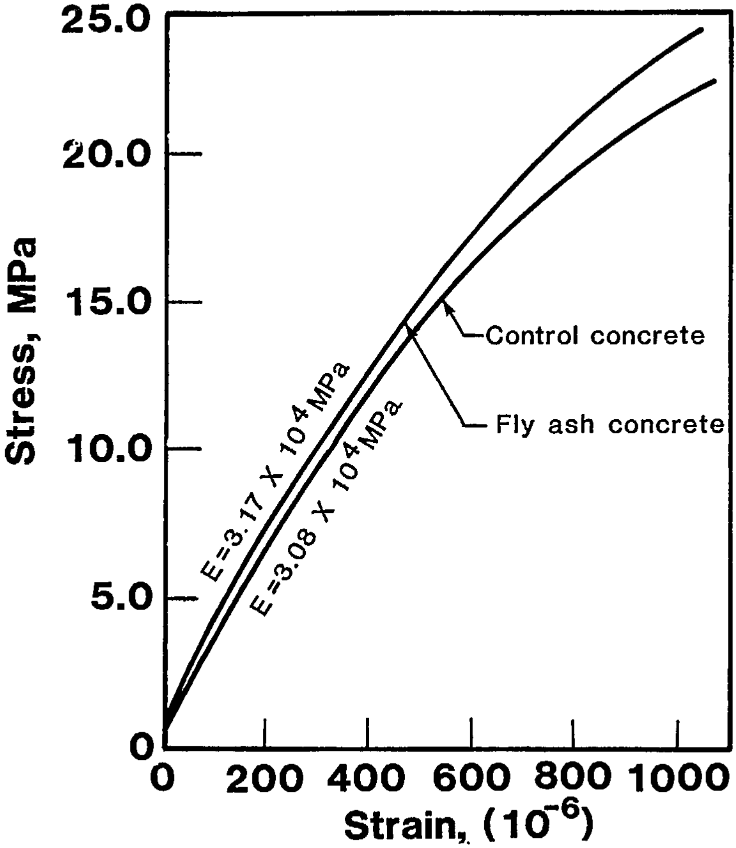

Fig. 4.6 — Stress–strain relationships for concretes (40)

Ghosh and Timusk (102), studied fly ash concretes, proportioned for equivalent 28-day strength, over a range of nominal strength values. They showed the relationship between strength and modulus of elasticity reproduced in Figure 4.7 and concluded that for all strength levels the modulus of elasticity of fly ash concrete is generally equivalent to that of the reference concrete. In all instances, the modulus was found to exceed that given by the ACI formula.

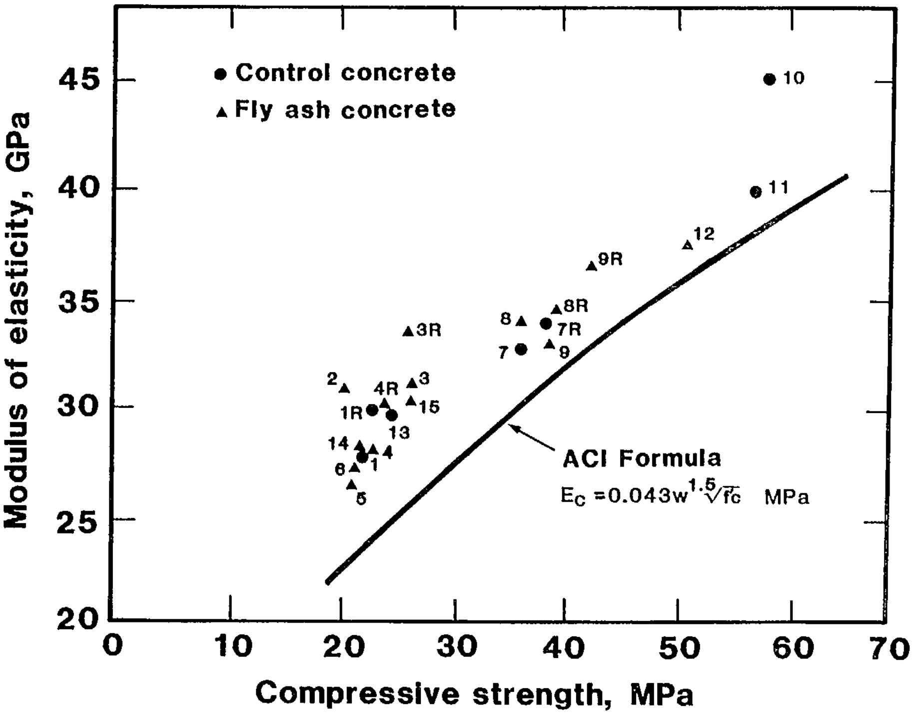

Fig. 4.7 — Moduli of elasticity of fly ash concretes (102)

Nasser and Marzouk (103) examined the effects of temperature on modulus of elasticity of concrete made from fly ash (from a Saskatchewan lignite source) and a sulphate resistant, ASTM Type V cement. They reported that over the range of temperature 21 to 232°C, the modulus of elasticity was reduced by up to 40% for specimens that were both sealed and unsealed to prevent moisture loss.

Effect of Fly Ash on Creep Properties of Concrete

Data on creep of fly ash concrete are limited. Lohtia et al. (104) have reported the results of studies of creep and creep recovery under stress–strength ratios of 20 and 35% of plain and fly ash concretes made by replacing cement with equal weights of fly ash in the range of 0 to 25%. From this work they drew the following conclusions:

- Replacement of 15% of cement by fly ash was found to be the optimum value with respect to strength, elasticity, shrinkage, and creep for the fly ash concrete studied.
- Creep-time curves for plain and fly ash concretes were similar with creep linearly related to the logarithm of time.
- Increase in creep with fly ash content up to 15% was negligible. However, slightly higher creep took place at fly ash contents higher than 15%.
- The creep coefficients were similar for materials with fly ash contents in the range of 0 to 25%.
- Creep recovery was found to vary from 22 to 43% of the corresponding 150-day creep. For cement replacement beyond 15%, the creep recovery was smaller. No definite trend of creep recovery as a function of stress–strength ratio was observed.

Among more recent studies, Ghosh and Timusk (102) have examined bituminous fly ashes of different carbon contents and fineness values in concretes at nominal strength levels of 20, 35, and 55 MPa (water-to-cement ratios 1.0, 0.4, and 0.2, respectively). Each concrete was proportioned for equivalent strength at 28 days. In the majority of specimens, it was found that fly ash concretes showed less creep than the reference concretes. This was attributed to a relatively higher rate of strength gain after the time of loading than for the reference concretes.

Yuan and Cook (83) reported the data in Figure 4.8 from studies of high-strength concrete containing a high-calcium fly ash, which showed fly ash concrete containing 30 and 50% ash to exhibit more creep than either the control concrete or a concrete with 20% ash. More extensive data from this study are discussed in Chapter 6 of this report in regard to the use of fly ash in high-strength concrete.

Gifford and Ward (105), examined lean mass concrete and concluded that fly ash reduces creep as a result of a number of factors including the following:

- Fly ash increases the elastic modulus.
- It contributes to the total aggregate and reduces the volume of paste available to creep.

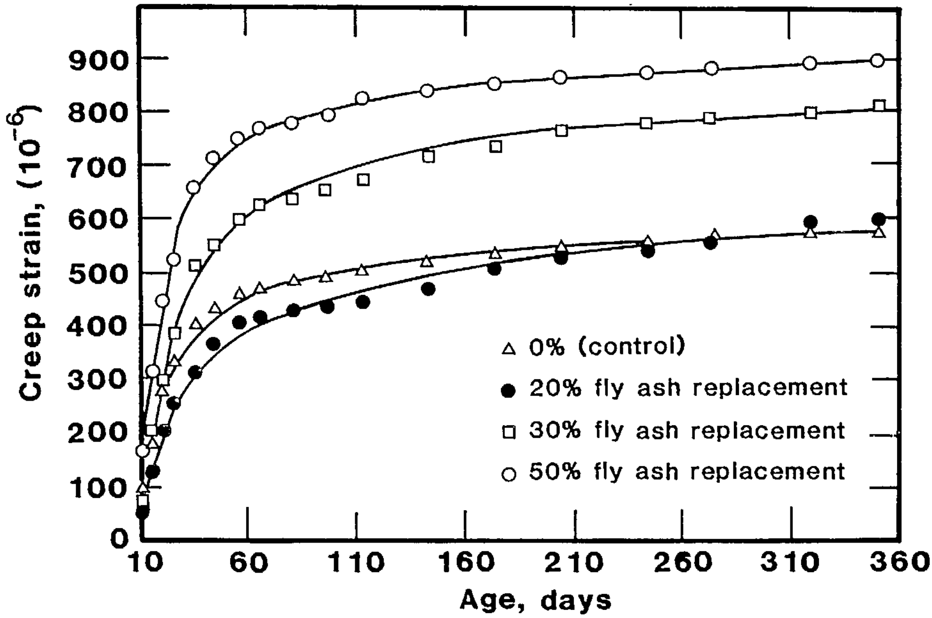

Fig. 4.8 — Creep of fly ash concretes (83)

Effect of Fly Ash on Load-Independent Volume Changes of Concrete

It has been generally reported that the use of fly ash in normal proportions does not significantly influence the drying shrinkage of concrete. Typical of the conclusions of most researchers in this respect are those made by Davis et al. (2) who comment as follows:

> "For masses of ordinary thickness, such as are normally found in highway slabs and in the walls and frames of buildings, the drying shrinkage at the exposed surfaces of concrete up to the age of one year is for fly ash cements about the same as, or somewhat less than, that for corresponding portland cements. At a short distance from the exposed surface the drying shrinkage up to the age of one year is substantially less for concretes containing corresponding portland cements.
>
> "For very thin sections and for cements of normal fineness the drying shrinkage of concretes containing finely ground high-early-strength cements may be somewhat reduced by the use of fly ash."

Figure 4.9 shows data presented by Elfert (62) comparing the drying shrinkage and autogenous length change of fly ash concrete with plain concrete and concrete made with other pozzolans. Typically, fly ash concrete performed better in these respects than the other concretes studied.

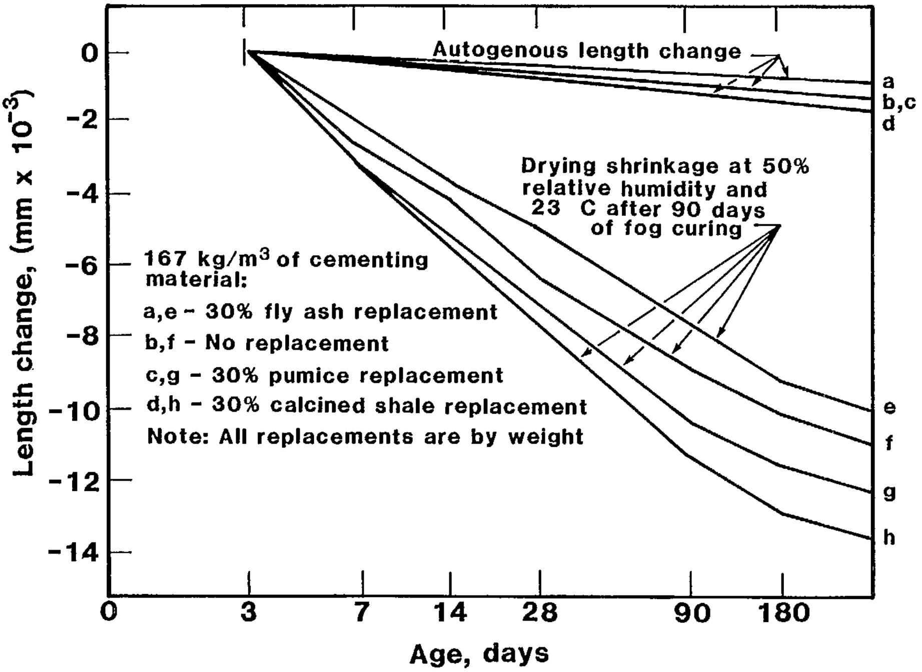

Fig. 4.9 — Drying shrinkage and autogenous length change for concretes containing various pozzolans (62)

In a more recent study, Ghosh and Timusk (102) showed that for the same maximum size of aggregate and for all strength levels, the shrinkage of concrete containing fly ash is lower than that for non-fly ash concrete.

In their studies of concrete using high-calcium fly ash, Yuan and Cook (106,83) concluded that the replacement of cement by fly ash has little influence on drying shrinkage. Their data are shown in Figure 4.10. Similar conclusions may also be drawn from the data on shrinkage obtained by CANMET (38) for concretes incorporating a range of fly ashes (Table 4.5).

Table 4.5 — Drying shrinkage of fly ash concretes*

Mixture No.**	Duration of drying, days	Shrinkage measurements: Initially cured for 7 days in water — Moisture*** loss, %	Drying shrinkage, x10^{-6}	Initially cured for 91 days in water — Moisture*** loss, %	Drying shrinkage, x10^{-6}
Control 2	224	55.0	422	53.7	453
F1	224	57.5	447	47.9	365
F2	224	57.3	364	45.4	280
F3	224	56.9	411	56.2	405
F4	224	54.7	379	49.2	387
F5	224	58.8	404	51.1	403
F6	224	60.6	475	56.4	454
F7	224	64.3	397	54.1	433
F8	224	56.3	400	—	327
F9	224	58.2	390	49.3	361
F10	224	58.4	642	55.2	500
F11	224	49.5	454	48.9	362

*From reference 38.
**See Tables 3.1 and 3.2 for fly ash and mix proportion data.
***As a percentage of total original water.

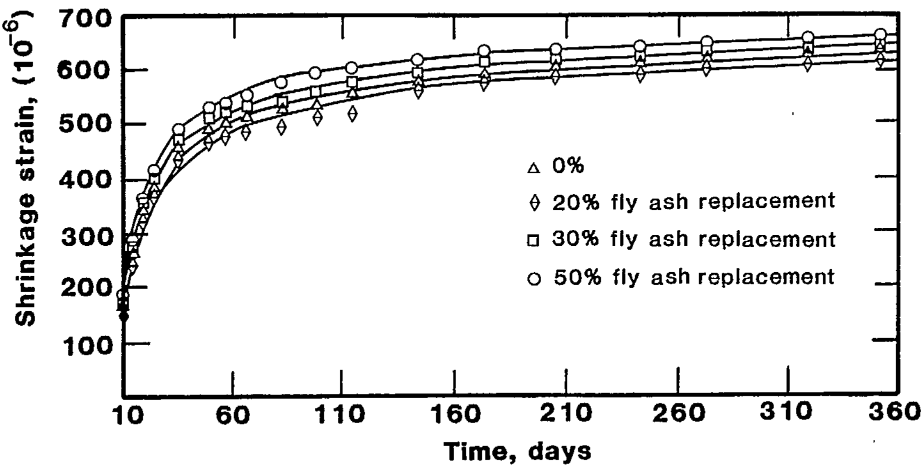

Fig. 4.10 — Drying shrinkage of concretes incorporating high-calcium fly ash (83)

Munday et al. (107) have reported typical shrinkage–age relationships for fly ash concretes as shown in Figure 4.11 and have concluded that a general relationship exists between drying shrinkage and equivalent cement content (Figure 4.12). It was also found that wetting and drying of fly ash concrete resulted in a cumulative expansion over a number of cycles (Figure 4.13). It was concluded that overall, the incorporation of fly ash does not significantly affect the drying shrinkage, wetting/drying expansion, or thermal expansion of concrete.

Thermal expansion of concrete is mainly affected by the thermal expansion of the coarse aggregate that constitutes its main component. Values for wet limestone and quartzite have been reported to be 4.0 and 11.7 micro-strain per °C, respectively, and cement paste is reported to vary from 11.0 to 20.0 micro-strain per °C (105). Gifford and Ward (105) quote Dunstan as suggesting that fly ash slightly reduces thermal expansion; their own data indicated an average reduction of 4% at a fly ash level of 40%.

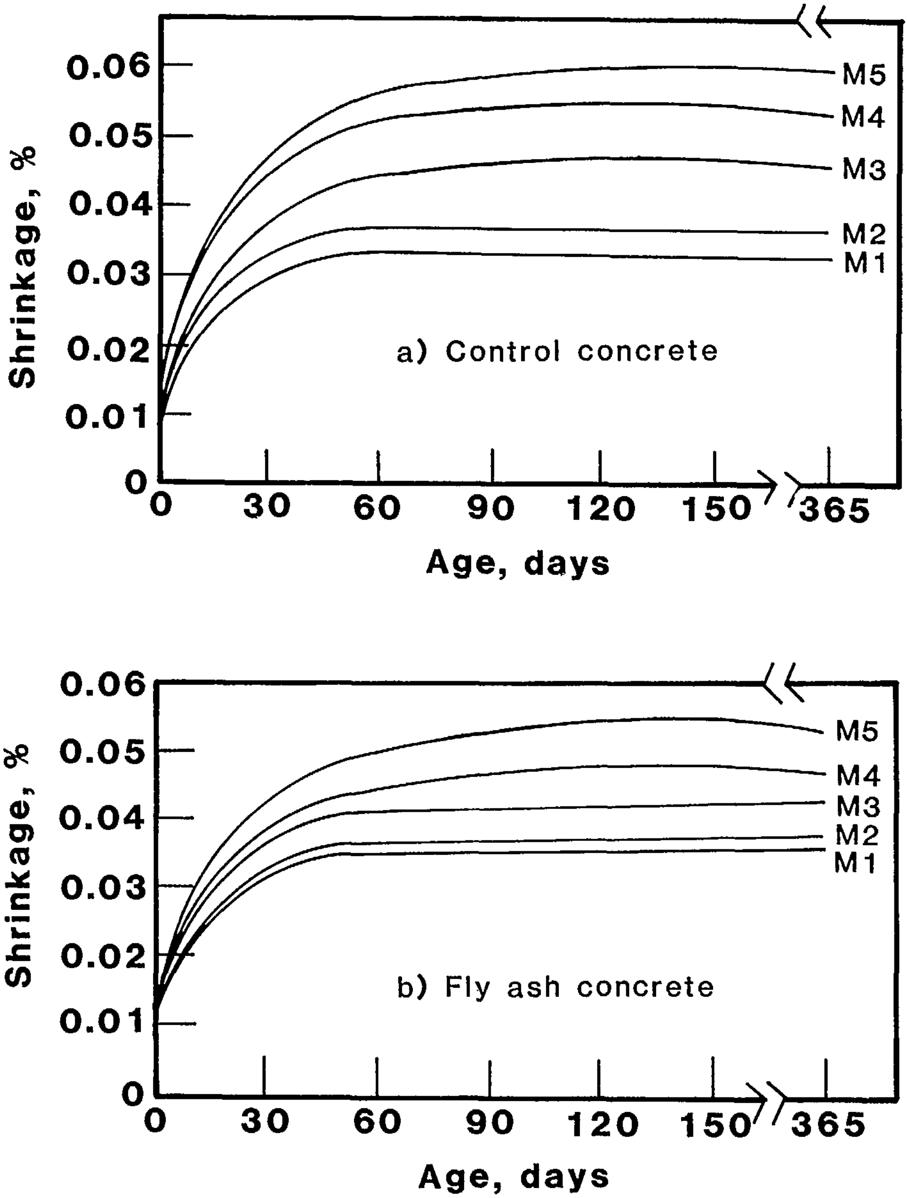

Fig. 4.11 — Drying shrinkage of concretes incorporating low-calcium fly ash (107)

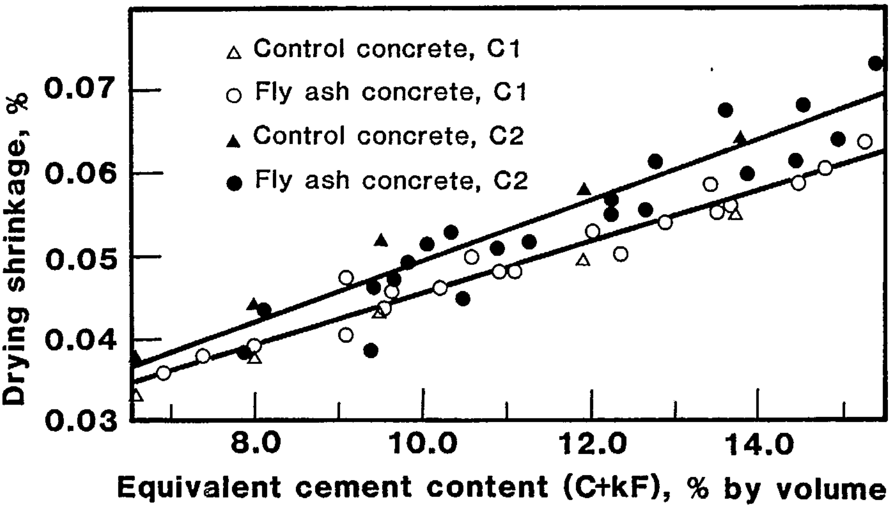

Fig. 4.12 — Drying shrinkage of concretes versus equivalent cement content (107)

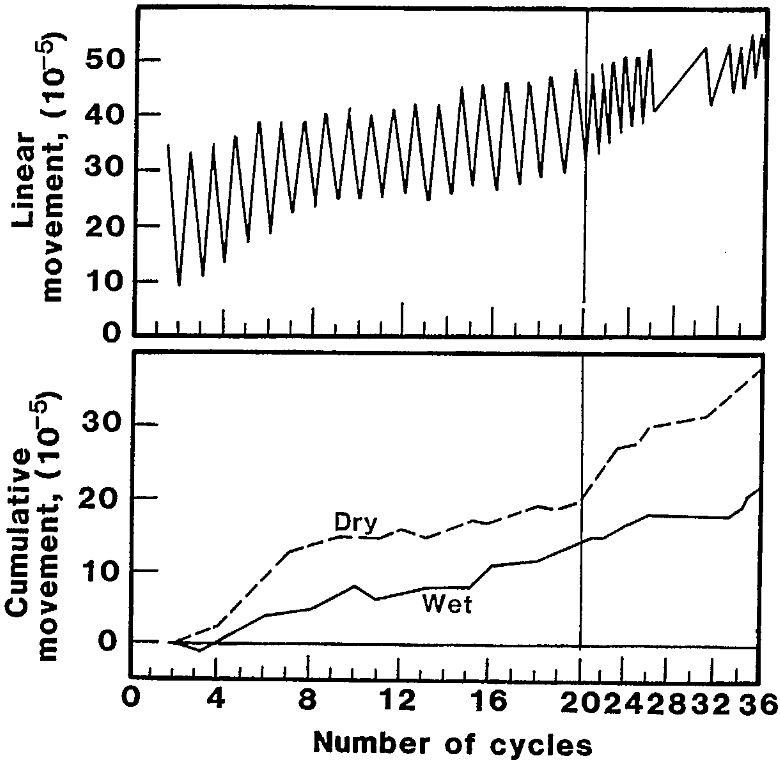

Fig. 4.13 — Wetting and drying movements of fly ash concretes (107)

5. USE OF FLY ASH IN CONCRETES FOR SPECIALIZED APPLICATIONS

"The use of a good quality fly ash, meeting the specifications of ASTM C618 (Class F)... is a must in the production of high-strength concrete." — Blick, Petersen, and Winter (108).

For most construction applications, the decision whether to use fly ash in concretes will be made largely on the basis of the availability of materials, local concrete practice and, most importantly, economics. There are, however, some types of special concretes that require the use of fly ash or other mineral by-products to attain specified properties. In particular, high-strength concretes (>50 MPa at 28 days) and roller-compacted mass concretes both depend on the use of fly ash for their structural and economic success.

High-Strength Concrete

High-strength concretes can be classified broadly into three groups:

- — concretes in the strength range from 35 to 70 MPa used over the past ten years in a number of construction applications;
- — concretes ranging in strength from 70 to 100 MPa;
- — concretes with compressive strength in excess of 100 MPa.

As Wolsiefer has noted (109), although field-placeable concrete in the strength range from 70 to 120 MPa is now commercially available, the major documented uses of high-strength concrete in building applications have been for 62 MPa concrete in the Chicago area. Thus, for the present time, consideration of the use of fly ash in high-strength concrete must be restricted to the lower end of the above strength range.

High-strength concrete is used for a number of reasons, the most important being:

- — to minimize the size of concrete structural members in buildings;
- — to obtain more rapid production cycles in the pre-cast and prestressed concrete industry;
- — to obtain high strength and modulus of elasticity in structural members built to withstand large stresses.

In general, the production of high-strength concrete requires the use of low water-to-cement mixes with sufficient workability to permit placement in a heavily reinforced structure. To meet these requirements, the following factors are usually considered important (108,110):

- use of high cement contents (up to 550 kg/m^3) at slumps of 75 to 100 mm;
- stringent selection of cement and aggregates;
- use of low water-to-cement ratios, attained through the employment of water-reducing agents and superplasticizers (see Chapter 6);
- use of pozzolans, especially fly ash.

Fly ash functions in high-strength concrete to provide at least two benefits:

- A good-quality fly ash generally will permit the water content of a concrete mix to be reduced without loss of workability (see Chapter 2).
- Fly ash produces increased strength at late ages of curing that cannot be achieved through the use of additional portland cement.

Typical mix proportions for high-strength concrete used in two structures built in the Chicago area during the 1970's are given in Table 5.1; the resulting compressive strength values obtained with these mixes are given in Table 5.2. Concrete mixes incorporating fly ash and using similar proportions, with strengths of 55 MPa, have been used in construction in the Toronto area (111).

Table 5.1 — Mix proportions and properties of fresh high-strength concretes*

	Quantity/m^3	
Material	Water Tower Place	River Plaza
Cement (kg)	383.7	385.6
Fine aggregate (kg)	464.9	471.7
Stone (kg)	816.5	784.7
Water (kg)	136.1	149.7
Water-reducing admixture (mL)	751.1	1271.5
Fly ash (kg)	45.4	45.4
Slump (mm)	114.3	114.3
Air content (%)		1.5
Unit weight (kg/m^3)	2433.4	2383.8

*From reference 108.

Table 5.2 — Compressive strengths of high-strength concretes*

Age (days)	Compressive strength, MPa					
	Water Tower Place			River Plaza		
	Air**	Moist	Cores	Yard	Jobsite	Cores
7		52.68			50.40	46.54
28	63.09	64.81		71.29	64.88	55.85
56	0	72.95		77.50	72.40	73.71
90	64.95			80.19	78.67	72.12
180	63.50			91.15		
365	66.88					
730	61.78		79.71			

*From reference 108.
**7 days' moist curing followed by curing at 50% RH, 21°C.

Table 5.3 — Mix proportions and properties of fresh and hardened high-strength concretes of constant ash/cement ratio*

	Nominal cement content, kg/m³				
	279	335	390	446	502
Materials, kg/m³					
Cement	282	341	396	449	501
Fly ash	71	85	99	112	131
Limestone	1144	1147	1141	1130	1121
Sand	735	643	578	513	454
Water	148	157	161	169	179
W/R admixture, mL/m³	696	851	967	1083	1238
Properties of fresh concrete					
Slump, mm	102	102	114	102	95
Unit weight, kg/m³	2379	2373	2376	2373	2374
W/(C+F)	0.42	0.37	0.33	0.30	0.28
F/C	0.25	0.25	0.25	0.25	0.26
Compressive strength, MPa					
7 days	44.3	48.1	53.1	55.1	59.3
28 days	54.6	62.7	67.4	72.7	70.2
56 days	61.0	68.0	75.7	75.9	78.0
90 days	63.3	68.9	75.0	75.7	75.0
180 days	67.8	76.9	83.6	86.6	85.3

*From reference 112.

Cook (112) has reported on a comprehensive investigation of concretes in the strength range from 50 to 75 MPa (28 days) made using a high-calcium fly ash (CaO = 30.3%). Data from related studies were presented in Chapter 4. Tables 5.3 and 5.4 illustrate how fly ash can contribute to the strength development of high-strength concretes and the flexibility in selection of mix proportions that can be used to obtain essentially similar concretes. In Table 5.3, the concrete properties attained by using different quantities of cementitious materials at a constant ash-to-cement ratio (0.25) are presented. As the cement factor was increased, sand content and the water-to-cementitious material ratio was reduced. Strength at 28 days could be controlled over a range of 55 to 70 MPa. The data in Table 5.4 show the effect on strength (28 days) of increasing fly ash content from 20 to 30% for two basic concrete mixes.

Table 5.4 — Mix proportions and properties of fresh and hardened high-strength concretes at various ash/cement ratios*

	Mix number			
	1	2	3	4
Materials, kg/m^3				
Cement	320	281	279	245
Fly ash	80	120	71	105
Limestone	1127	1127	1127	1127
Sand	698	702	769	720
Water	151	142	148	145
Admixture**				
Mix properties				
Slump, mm	102	95	83	108
W/(C+F)	0.38	0.36	0.42	0.41
F/(C+F)	0.20	0.30	0.20	0.30
Compressive strength, MPa				
7 days	44.9	44.0	42.0	40.5
28 days	56.6	55.8	52.7	52.3
56 days	58.6	61.9	56.8	58.8
180 days	68.9	74.4	70.5	71.6

*From reference 112.
**Quantities not reported.

Roller-Compacted Concrete

In the 1970's, a method for the construction of dams termed *roller compaction* was proposed (113-116). The method, which in many ways is more related to the procedures used in geotechnical engineering than to conventional concrete practice, depends upon the placement of layers of a low-workability concrete in the interior of a dam and its compaction using vibratory rollers.

The American Concrete Institute (117) describes roller-compacted concrete (RCC) as a dry concrete material that is consolidated by external vibration using vibratory rollers. It differs from conventional concrete in its required consistency, in that for effective consolidation RCC must be dry enough to support the weight of the placement equipment, but fluid enough to permit distribution of the paste throughout the mass during mixing and compaction.

Roller-compacted concrete must satisfy four requirements:

- It must have a high density with a minimum of air voids.
- The layers of concrete must bond together (116).
- The generation of heat in the dam must be minimized.
- The hardened concrete must have a high capacity to withstand tensile strains to resist thermal cracking.

Three types of materials have been investigated and used for RCC:

- cement-stabilized, soil-like materials;
- lean concrete, with a cementitious content of 100 to 150 kg/m^3, of which up to 30% may be fly ash;
- rich concrete, with a cementitious content of 180 to 270 kg/m^3 of which 60 to 80% may be fly ash.

Roller-compacted concretes can be made from any of the basic types of portland cement in combination with pozzolans. In regard to proportioning, the principal difference between the selection of the relative quantities of the cementitious components in RCC as compared to more conventional concretes relates to the use of large quantities of fly ash.

The principal function of fly ash in RCC is to occupy space between larger particles by providing a large volume of fine material that would otherwise require the use of additional cement.

Roller-compacted concrete is normally required to have a high paste content. Dunstan (118) has shown that as the paste-to-mortar ratio falls below 0.35 to 0.38, the density of the compacted mass is significantly reduced. Below this level of paste content, all the voids in the fine aggregate are not being filled. To obtain maximum density, the paste content must be increased; however, to attain this by the addition of portland cement results in two serious disadvantages:

- The rate of heat evolution increases and the possibility of thermal cracking becomes greater.
- The cost of the concrete may be become uneconomical.

The desired approach to obtain maximum density RCC is to use large volumes of fly ash to increase the paste content.

Pozzolanic activity is somewhat secondary, in that strength in RCC can develop over long periods after placement. As the ACI Committee report states (117):

> "Where there is a deficiency in fines (in RCC) a pozzolan does not have to be highly reactive to be effective. Thus, many fly ashes whose reactivity, due to insufficient particle fineness, would not meet... ASTM specifications would be suitable for most roller compaction applications."

Typical RCC mix proportions and corresponding strength data, as reported by ACI Committee 207, are shown in Tables 5.5 and 5.6.

Table 5.5 — Mix proportions for some roller-compacted concretes*

		Mix data, kg/m³				
Source	Maximum aggregate Size, cm	Cement	Pozzolan	Water	Fine aggregate	Coarse aggregate
1	7.6	56	77	77	60	1649
2	11.4	139	0	80	618	1774
3	7.6	139	0	86	683	1691
4	7.6	139	0	83	676	1602
5	7.6	42	78	83	676	1602
6	3.8	75	164	89	745	1426
7	3.8	45	178	84	727	1438
8	3.8	116	139	103	657	1438

*From reference 117.

Table 5.6 — Properties of some roller-compacted concretes*

Source	Age, days	Compressive strength, MPa	Shear strength, MPa	
			Mass	Joint
1	138	23	4	2
2	72	26	5	1
3	66	23	6	
4	120	23	6	3
5	120	16	4	1
6	90	26		3
7	90	18	2	2
8	90	41		

*From reference 117.

As in more conventional mass concrete, fly ash contributes to reducing the rate of heat evolution and, hence, the extent of temperature rise.

Permeability of roller-compacted concrete used in the Upper Stillwater Dam was reported to be equal to, or less than, conventional mass concrete (119).

Both air-entraining and water-reducing admixtures have been used at normal dosages in roller-compacted concrete. ACI committee 207 (117) states that these admixtures are effective in reducing the vibration time for full consolidation. However, the effectiveness of air-entraining admixtures in roller-compacted concrete and the appropriate dosage rates are as yet not established.

The use of roller-compacted concrete is not restricted to mass structures such as dams. It has been employed to replace rip-rap for erosion control of a floodway sill in Alaska, as a foundation rock protection, in a lock floor, and in other structures (120).

As Joshi (121) has pointed out, roller-compacted concretes are closely related to the family of *stabilized materials* commonly used for pavements and other applications. The use of roller-compacted and lean concrete containing high amounts of fly ash has been extensively studied for pavement construction in Britain. Sherwood and Potter (122) have reported studies of *ash-modified lean concrete* for use in road-bases. They suggest that ash-modified lean concrete should be equal in performance to conventional lean concrete provided that the development of thermal and shrinkage cracks was similar and that it could withstand repeated traffic-induced stress at early ages.

Dunstan (118) has reported on field applications of lean concretes containing high amounts of fly ash and drew the following conclusions:

- A considerable material cost saving (over 20%) was achieved.
- Good quality control over the batching process is required to maintain consistent material.
- It is difficult to obtain satisfactory levels of air-entrainment in concrete incorporating large quantities of fly ash.
- Very little early-age cracking was seen in the base materials.
- A fly ash that did not conform to British Standard specifications was found to be adequate with no deleterious effects.

With regard to air-entrainment, Oliverson and Richardson (119) noted that research on the freezing and thawing durability of roller-compacted concrete is needed. Certainly, given the well-known difficulties associated with air-entrainment of some fly ash concretes, considerable research of this issue is required if roller-compacted concrete is to find use under the climatic conditions to which most pavement concrete is exposed in Canada.

6. FLY ASH CONCRETE INCORPORATING CHEMICAL ADMIXTURES AND MINERAL BY-PRODUCTS

"All indicators point to a promising future for (mineral admixtures) ... Further investigation of the interaction of water-reducing admixtures and high-range water-reducing admixtures (superplasticizers), can enhance the value of both of these classes of products." — Richard C. Mielenz, 1983.

In recent years, the use of chemical admixtures and mineral by-products, such as slags and condensed silica fume, has become relatively common. If fly ash is used in concrete, its interaction with, or influence upon, the efficiency of other *admixtures* must be considered. This chapter examines interaction of fly ash with other materials used to modify concrete properties.

Chemical Admixtures

In concrete technology, the term *chemical admixtures* is used to describe soluble substances excluding air-entraining admixtures that are used as ingredients of a concrete mix to modify its properties. Most chemical admixtures react with cement. They may be classified into four groups:

- ***Retarders*** include many organic and inorganic compounds, frequently derived from industrial by-products related to lignosulphonates.
- ***Accelerators*** are mostly inorganic salts of calcium or alkali metals, the most common being calcium chloride.
- ***Water reducers*** include a very broad range of surface-active agents, with or without set-retarding capacity, based upon lignosulphonates and hydroxy-carboxylic acids. Their main function is to disperse and deflocculate cement particles.
- ***Superplasticizers**** fall into one of the following classes:
  - sulphonated melamine-formaldehyde condensates
  - sulphonated naphthalene-formaldehyde condensates
  - modified lignosulphonates
  - other surfactants.

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*Also termed high-range water reducers.

In spite of their importance in concrete technology, with the exception of superplasticizers, very little direct study has been made of the interactions of most chemical admixtures with fly ash. In the case of superplasticizers, their use in high-strength concrete (see Chapter 5) has been closely involved with the use of fly ash and, hence, more information is available on their mutual compatibility.

In general, the concern with regard to possible fly ash/admixture interactions results from the experiences that have been commonly reported on the interference of fly ash and other finely divided particulates with the efficiency of air-entraining agent activity in fresh concrete (see Chapter 3). Because of the generally accepted view that air-entraining agents are adsorbed on fine particulates other than cement, it is not unreasonable to anticipate that similar problems may arise with other admixtures that rely on surface activity for their effect.

In the case of superplasticizers, this issue has been studied directly (123,124). Uchikawa et al. (123) have reported that, for three types of superplasticizers examined, adsorption on fly ash was less than on cement in water suspensions. This was attributed to differences in the surface properties. The fly ash used was of a low-calcium type and, hence, the results should not be considered to be generally applicable to all fly ash types.

Nagataki et al. (124) examined the adsorption of a naphthalene-type superplasticizer on several fly ashes of different carbon contents. The authors reported that the adsorption of superplasticizer appears to be reduced in the presence of carbon, in clear contradiction to the reported behaviour of air-entraining agents (see Chapter 3).

Contrary observations were reported by Uchikawa et al. (125) for two classes of anionic surfactant superplasticizers and five low-calcium fly ashes in direct comparison with air-entraining agents. The results from this study indicate some degree of inter-dependence between the carbon content of a fly ash and its capacity to adsorb superplasticizers.

It is clear from the generally contradictory nature of the reported data that much research remains to be done on the interaction of surfactants with fly ash and the consequent effects on the efficiency of chemical admixtures in fly ash concrete.

Accelerators

Mailvaganam, Bhagrath, and Shaw (41) have reported studies of the effects of chloride and non-chloride accelerators and a superplasticizing admixture on fly ash concretes cured at two different temperatures. Their data, shown in Tables 3.1 (Chapter 3) and 6.1 indicate that both chloride and non-chloride accelerators are effective in the presence of fly ash. They do not, however, completely compensate for the slow rate of early strength development that results from the use of simple substitution of ash for cement on an equal quantity basis.

Water-reducing admixtures

In 1962, the U.S. Corps of Engineers reported (126) work in which fly ash and water-reducing admixtures were combined in making special concrete structures. It was concluded from compressive and flexural strength determinations and estimated costs that such structures could be made more economically with these materials than with portland cement alone.

In 1971, Lovewell and Hyland (127) concluded from research and literature surveys that:

> "...combinations of pozzolans (including fly ash) with water-reducing agents, or with water-reducing-retarder agents, with and without air-entrainment can be used in concrete without creating abnormalities. All such ingredients should be checked for compliance with applicable standards and trial mixes should be made to check compliance of such mixes with specified quality parameters."

In 1975, Samarin and Ryan (128) reported studies made on fly ash concretes proportioned by the replacement–addition method and containing water-reducing admixtures. Two series of concrete trial mixes were reported: Series A in which a comparison was made between plain, fly ash, admixture, and fly ash plus admixture concretes of comparable consistency and compressive strength: Series B in which a comparison was made between plain and fly ash plus admixture concretes of three different strength levels. The comparative data from this research are given in Tables 6.2 and 6.3. From this work, Samarin and Ryan concluded as follows:

— "As compared with plain mix, concrete containing fly ash and lignin-based admixture is expected to give:

i) higher ninety-day strength

ii) comparable workability

iii) lower bleeding capacity in leaner mixes, slightly reduced modulus of elasticity at twenty-eight days

v) comparable, or lower, ninety-day shrinkage

vi) setting times extended by one to two hours.

— "As compared with admixture mix, fly ash-admixture concrete is expected to give:

i) comparable ninety-day strength
ii) improved workability
iii) slightly lower bleeding capacity
iv) improved indirect tensile strength at twenty-eight days
v) comparable, or lower, ninety-day shrinkage
vi) comparable setting times.

— "As compared with fly ash mix, fly ash-admixture concrete is expected to give:

i) comparable ninety-day strength
ii) comparable workability
iii) comparable bleeding capacity
iv) comparable indirect tensile strength at twenty-eight days
v) comparable ninety-day shrinkage
vi) setting times extended by one to two hours."

Table 6.1 — Properties of fly ash concretes incorporating chemical admixtures*

		Compressive strength (MPa)				Shrinkage % × 10^{-3}	
Mix***	Admixture**	3 days	7 days	28 days	90 days	28 days	56 days
1	—	23.3	28.5	35.4	41.1	86	100
2	—	13.1	16.8	24.6	36.1	92	103
3	CL	29.7	35.3	40.5	46.9	89	106
4	CL	16.6	20.9	30.9	40.1	94	106
5	MFS	32.6	36.9	43.0	47.2	102	112
6	MFS	18.0	21.6	30.2	41.4	99	120
7	NCL	26.3	31.0	37.5	42.7	82	98
8	NCL	14.6	18.5	26.7	38.3	87	95

*From reference 41.
**CL = Chloride accelerator (1.5% active solids).
MFS = Superplasticizer (0.6% active solids).
NCL = Non-chloride accelerator (0.68% active solids).
***See Table 3.3 (Chapter 3).
All at a dosage of 3% by weight of cementitious material.

Table 6.2 — Compressive strengths of water-reduced concretes*

	Compressive strength (MPa)			
Mix type	3 days	7 days	28 days	90 days
Series A				
Plain	25.4	30.1	40.6	41.6
Fly ash	23.8	31.1	44.6	49.8
Admixture	22.8	31.5	41.3	44.6
Fly ash admixture	20.5	28.5	39.8	49.5
Series B				
Plain	31.3	34.2	47.5	54.7
Fly ash admixture	28.7	35.4	47.5	56.4
Plain	26.0	30.5	41.5	46.5
Fly ash admixture	21.3	29.0	39.7	52.0
Plain	13.7	18.9	27.5	31.6
Fly ash admixture	13.3	19.0	30.4	42.7

*From reference 128.

Table 6.3 — Properties of concretes incorporating cement, fly ash, and water-reducing admixtures*

Series	Mix type	Cementitious content, wt %		Water demand kg/m³	Slump mm	Air %	Bleeding capacity kg/m²	Setting time (h:min)		Strength — Compressive 28 day	Strength — tensile 28 day	Modulus of elasticity 10⁴ × MPa
		Portland	Total					Inititial	Final	MPa	MPa	
A	P	15.2	15.2	188	80	3.1	2.5	4:45	6:45	40.6	3.95	3.65
	F	14.1	16.7	182	90	2.3	2.2	4:40	6:15	44.6	4.38	3.61
	A	13.7	13.7	165	80	5.7	2.1	6:20	8:30	41.3	4.00	3.52
	F-A	13.1	15.7	170	80	5.2	2.0	6:30	9:05	39.8	4.10	3.41
B	P	19.1	19.1	196	80	2.4	0.9	4:10	5:35	47.5	4.49	3.68
	P	15.2	15.2	185	85	2.8	2.4	4:40	6:15	41.5	4.52	3.50
	P	12.2	12.2	193	80	3.8	4.9	5:30	7:30	27.5	3.56	2.98
	F-A	17.0	19.1	173	80	5.2	1.4	6:10	7:55	47.5	4.70	3.55
	F-A	13.1	15.7	169	80	5.3	2.5	6:30	8:25	39.7	3.78	3.30
	F-A	9.8	13.1	167	80	5.8	4.3	6:55	8:50	30.4	3.37	3.18

*From reference 128.

Superplasticized concretes

During the past few years, there has been an increase in the use of superplasticizing admixtures for one of three purposes:

- — to increase the fluidity of fresh concrete proportioned with *normal* water-to-cement ratios, and thus to produce what has been termed flowing concrete;
- — to permit reduction in the cement content of concrete while maintaining the same water-to-cement ratios;
- — to reduce greatly the quantity of water used while maintaining the same cement content and slump, thus achieving very low water-to-cement ratios.

To correctly proportion flowing concrete (concrete with slump in excess of 180 mm), it is desirable to use more sand than is employed in conventional concrete. However, it has been found that instead of incorporating excessive amounts of sand, it is preferable to use fly ash to provide the necessary fine particles that give cohesiveness to the mixes (129). It is to be expected that there will be an increased use of fly ash in the future for this application.

From an extensive laboratory study of the combined use of fly ash with superplasticizers, Lane and Best (130) have drawn the following conclusions:

- — "...superplasticizers are compatible with fly ash in concrete and produce no detrimental effects. The benefits claimed for these admixtures in plain concrete, however, were not as apparent in fly ash mixtures, particularly with respect to compressive strength gains and duration of increased plasticity. Water reductions for equal slump did not exceed 15 per cent, improving this characteristic only slightly over a standard water-reducing agent. The low water reductions can be attributed to the lower water requirement for fly ash concrete as compared to plain concrete for equal consistencies. Since there is less excess water initially available, the addition of water reducers is less effective.

- — "...superplasticizers are equally effective in attaining a temporary increase in concrete consistency for both fly ash concrete and plain concrete. The highly plastic phase diminishes after 15 minutes and ceases after about 30 minutes with fly ash concrete."

Ericksen and Nepper-Christensen (131) examined the water-reducing effects of a sodium naphthalene sulphonate superplasticizer on concretes incorporating two low-calcium fly ashes. They reported higher levels of water reduction than those found by Lane and Best (130). This was attributed to the higher cement content and larger dosage of admixture used in their study.

Brooks et al. (132) compared the behaviour of four concrete mixes:

- — plain
- — plain with superplasticizer
- — fly ash
- — fly ash with superplasticizer.

The mix proportions used for this study, which were selected to produce a minimum strength at 28 days of 30 MPa with a slump of 40-60 mm, are shown in Table 6.4. Compressive strength development largely reflected the effects of water reduction (Table 6.5) for both plain and fly ash concretes.

Swamy et al. (133) reported the data shown in Table 6.6 for flowing concrete (slump 260 to 280 mm) containing fly ash and proportioned to give compressive strengths at one day comparable to plain concrete. The advantageous effects of moist curing versus air curing on the strength development of fly ash concretes is clearly seen from these data.

Table 6.4 — Mix proportions for superplasticized concretes*

Mix number	1	2	3	4
Cement, kg/m^3	314	314	219	219
Fly ash, kg/m^3			117.5	117.5
Aggregate/cement ratio	5.98	5.98		
Aggregate/cement + fly ash			5.58	5.58
Per cent fines	33.3	33.3	31.1	31.1
Water/cement ratio	0.57	0.48		
Water/cement + fly ash			0.46	0.35
Admixture % by weight of cement		1.60		
Admixture % by weight of cement + fly ash				1.60

Mix 1 = plain concrete.
Mix 2 = plain concrete with admixture.
Mix 3 = fly ash concrete.
Mix 4 = fly ash concrete with admixture.
*From reference 132.

Table 6.5 — Properties of superplasticized concretes*

Property	Units	Mix Number 1	2	3	4
Compressive strength	MPa				
1 day		13.0	19.0	11.0	18.5
7 days		37.5	50.5	31.0	39.5
28 days		48.5	61.0	44.5	53.0
Indirect tensile strength	MPa				
1 day		1.15	1.75	0.85	1.15
7 days		2.90	2.70	2.35	2.20
28 days		3.35	3.65	3.05	2.75
Static modulus of elasticity	GPa	34.0	34.0	31.5	37.0
Secant modulus of elasticity	GPa	31.0	37.5	31.0	35.0
Volume changes-water stored	10^{-6}				
Creep		199	221	283	107
Swelling		25	37	123	39
Volume changes-air stored	10^{-6}				
Creep		424	419	305	227
Shrinkage		400	485	506	584

*From reference 132.

Table 6.6 — Properties of flowing concrete*

Curing regime	Slump (mm)	Age (days)	Compressive strength (MPa)	Flexural strength (MPa)
Air	265	1	12.0	1.8
		3	26.4	2.7
		8	36.1	3.3
		28	45.2	3.5
		43	50.8	4.1
3 days water and air	280	1	10.4	1.7
		3	24.6	3.0
		8	34.4	3.4
		28	48.0	4.3
		43	55.0	4.4

Mix proportions, kg/m^3.

Cement	287
Fly ash	123
Sand	758
Gravel	881
Water	191

Superplasticizer added at 2.5% by weight of cement + fly ash.
*From reference 133.

Mukherjee, Loughborough, and Malhotra (134) have examined the use of superplasticizers to aid the incorporation of large percentages of fly ash into high-strength concrete. Three types of superplasticizers were examined:

— superplasticizer M, a sulphonated melamine-formaldehyde condensate;

— superplasticizer N, a sulphonated naphthalene-formaldehyde condensate;

— superplasticizer L, a modified naphthalene-formaldehyde condensate.

The setting time, slump, density, and air content were determined for fresh concrete and the strength, elasticity, shrinkage, and creep were examined for hardened concrete specimens. The properties reported are presented in Tables 6.7 and 6.8. The experimental data were reported in relation to a reference fly ash concrete, proportioned to contain 37% fly ash and produce a compressive strength of 40 MPa at 28 days.

The following factors were noted:

— Satisfactory high-strength concrete can be obtained using large quantities of fly ash (low-calcium) and various superplasticizers.

— The mechanical properties of the water-reduced, superplasticized fly ash concrete were superior to the reference concrete.

— The workability may impose a limitation on its use for cast-in-place construction, due to a *gluey* texture at slumps between 65 and 75 mm.

— Superplasticizers N and L both increased the setting time markedly. It is not possible from the data to determine whether fly ash also influenced set-time. However, the data from Mailvaganam et al. (41) showed increases of 25% when melamine-formaldehyde sulphonate superplasticizer was used with fly ash in comparison with its use in a plain concrete mix.

Table 6.7 — Mix proportions and properties of high-strength concrete*

Mix	Batch	Mix proportions, kg/m³							Properties of fresh concrete		
		Cement	Fly ash	Fine aggregate	Coarse aggregate	Water	W/(C+F)	P**	Slump (mm)	Air*** (%)	Initial set h:min
1	1	377	223	420	1105	208	0.35		65	1.5	4:40
	2	378	224	420	1107	208	0.35		70	1.5	4:40
	3	377	223	420	1105	208	0.35		65	1.4	4:40
	4	377	223	419	1103	209	0.35		65	1.4	4:40
2	1	389	230	433	1139	171	0.28	M 1.97	75	1.5	4:25
	2	388	230	432	1137	171	0.28	1.97	70	1.7	4:25
	3	390	231	434	1141	172	0.28	1.97	65	1.6	4:25
	4	389	230	433	1139	171	0.28	1.97	65	1.6	4:25
3	1	390	231	434	1141	172	0.28	N 0.86	70	2.0	5:15
	2	391	231	435	1145	172	0.28	0.86	70	1.8	5:15
	3	389	230	433	1139	171	0.28	0.86	70	1.9	5:15
	4	390	231	434	1143	172	0.28	0.86	70	1.9	5:15
4	1	390	231	434	1143	172	0.28	L 2.70	75	1.6	7:40
	2	391	231	435	1145	172	0.28	2.70	75	1.4	7:40
	3	390	231	434	1143	172	0.28	2.70	75	1.5	7:40
	4	389	230	433	1139	171	0.28	2.70	75	1.6	7:40

*From reference 134.
**P = % superplasticizer by weight of cement + fly ash.
***Entrapped air only.

Table 6.8 — Properties of hardened superplasticized concrete*

Mix	Batch	Compressive strength of concretes, MPa (days) 7	28	56	91	183	365	Flexural strength 28 day MPa	Modulus of elasticity 28 day MPa × 10^4	Shrinkage after 448 days dry storage: Shrinkage %	Moisture loss %
1	1		41.0		51.8			6.3	3.17	−0.0441	1.83
	2	28.8	37.9	51.9	51.5				3.43		
	3	25.0		41.4				6.8		−0.0453	1.84
	4					53.4	57.3				
2	1		53.3		65.2			8.3	3.48	−0.0413	1.19
	2	36.1	52.5	61.8	65.6				3.46		
	3	36.1		57.7				8.0		−0.0399	1.13
	4					70.0	69.8				
3	1		52.5		66.9			8.0	3.48	−0.0467	1.07
	2	36.8	53.8	61.7	67.1				3.46		
	3	36.8		63.2				7.4		−0.0427	
	4					66.3	74.7				1.08
4	1		51.0		62.7			7.8			1.19
	2	35.4	51.0	59.5	62.5				3.45	−0.0455	
	3	34.1		59.0				8.1	3.45		1.26
	4					63.4	62.5			−0.0454	

*From reference 134.

Malhotra (135) examined the use of a sulphonated naphthalene-formaldehyde condensate superplasticizer in semi-lightweight concrete containing fly ash. The high strengths obtained at one day in the fly ash mixes (Table 6.9) were attributed to the combined effects of fly ash and superplasticizer in permitting extreme water reduction while retaining a practical level of workability.

Table 6.9 — Properties of semi-lightweight concrete incorporating fly ash and superplasticizer*

Mix proportions					Strength MPa	
Cement	Fly Ash kg/m³	Water	W/(C+F)	Superplasticizer % on wt of cement	1 day	28 day
422		137	0.33	0.49	27.1	43.5
431		124	0.29	0.90	34.1	47.0
445		110	0.25	1.50	35.0	49.6
393	60	113	0.25	1.20	36.0	47.6
420	30	112	0.25	1.40	38.2	48.5

*From reference I35.

Superplasticized concretes exhibit marked increases in slump; however, these increases are of short duration. Within 30 to 60 minutes after addition of superplasticizer the concrete reverts to its original consistency. This loss of slump presents some difficulties in the use of superplasticizers.

Ryan and Munn (136) have examined the effects of fly ash on slump loss. They investigated concrete mixes in which all or part of the cement was replaced by the same volume of fly ash. The data obtained indicated that the rate of slump loss was not greatly affected when the binder was a mixture of cement and fly ash, regardless of the relative proportions. However, when the concrete contains no portland cement, superplasticizer addition also reduced slump, but the rate of slump loss was greatly reduced. It was concluded that the superplasticizers examined are chemically affected by reaction with lime liberated during the hydration of portland cement in a way that leads to loss of plasticity in the mix.

In general, although there remain many unanswered questions, it is clear that the combined use of fly ash and superplasticizers or water reducers allows for a wider flexibility in the proportioning of concrete for fluidity, strength, or economy. The concretes so obtained should be of particular value for applications in situations where resistance to chemical and environmental attack is important.

Further research work is urgently required to establish both the nature of fly ash-surfactant interactions and their practical effects in concrete.

Mineral By-Products

In addition to fly ash, other mineral by-products have been used as supplementary cementing materials. Some, specifically ground-granulated blast furnace slag, have been used for many years in commercial concrete. Others, in particular condensed silica fume, have only recently been introduced and are largely in the developmental stages of application.

Slags develop strength in the presence of portland cement more rapidly than do most fly ashes. Furthermore, it is possible to substitute them for larger quantities of portland cement (up to 75-80%) while producing dense, durable concrete. Condensed silica fume is a very reactive pozzolan that develops high strength at low levels of substitution. Its main disadvantage is that, unlike fly ash, it causes a very marked reduction in workability and, hence, increases water demand.

Not unexpectedly, slags and condensed silica fume have been investigated as materials to be included with fly ash in concrete as a means of overcoming its two principal weaknesses:

- the relatively low level of cement substitution that is practical in structural concretes using fly ash;
- the relatively slow rate of strength development of fly ash concretes.

The combined use of slag and fly ash is not new. Ternary cements based on portland cement, granulated slag, and fly ash have been the subject of investigation (73,137-145) in a number of countries around the world and have been used on a commercial basis in France (137) and in Australia (146).

Combinations of condensed silica fume and fly ash in concretes are of more interest in that, at relatively high levels of fly ash substitution (30%) and low levels of condensed silica fume addition, considerable rates of early strength development are possible [Carette & Malhotra (147) and Mehta and Gjorv (148)].

Carette and Malhotra (147) have reported an extensive investigation of concretes containing cements made from 70% portland cement and 30% low-calcium fly ash, with additions of condensed silica fume in the range from 5 to 20%. Superplasticizer was used to compensate for the loss of slump consequent upon the use of condensed silica fume; in this way water content was kept constant.

Figure 6.1 shows typical strength development data for such concretes. The main features noted from this work were as follows:

- The quantity of superplasticizer required to maintain a constant slump increased as the quantity of condensed silica fume was increased.

— At 20% condensed silica fume, the rate of slump loss was rapid and the fresh concrete tended to be *gluey*.

— In general, regardless of the water-to-cementitious material ratio, strength at 1 and 3 days was higher for concretes incorporating condensed silica fume than for the control concrete (30% fly ash/70% portland cement) but lower than for an equivalent plain concrete.

— Pozzolanic action from the condensed silica fume was most apparent between 3 and 7 days; pozzolanic activity from fly ash became apparent after 28 days.

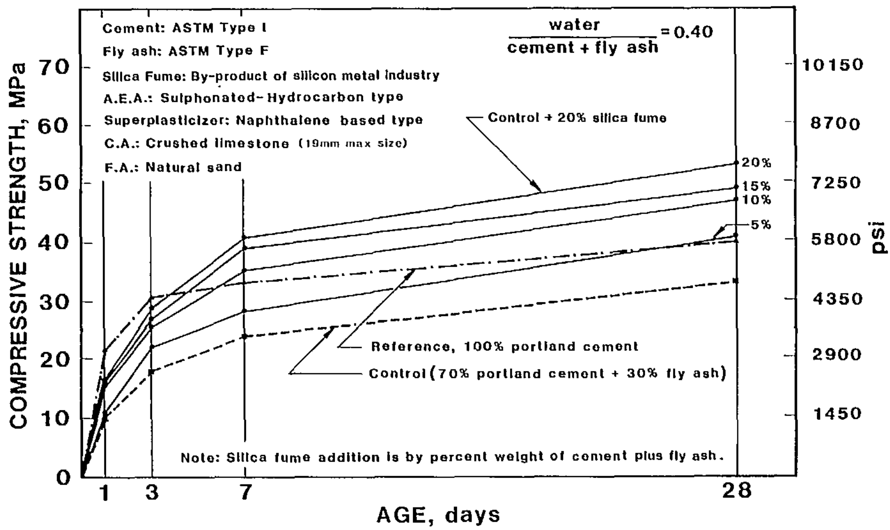

Fig. 6.1 — Compressive strength versus age for fly ash concretes with a W/(C+F) of 0.40, containing various additions of condensed silica fume (147)

The most important aspect of the combined use of fly ash and condensed silica fume in the types of concrete studied is that at ages beyond 7 days, the loss in compressive strength of concrete due to the incorporation of 30% of fly ash generally can be completely compensated by addition of as little as 10% condensed silica fume.

In view of the current interest in high-strength concretes and the desire, especially in the precast industry, for early strength development, it is to be expected that much more information will become available in the near future on the nature and performance of fly ash-condensed silica fume-portland cement concretes. Certainly, there is ample need for more research in this area where substantial cement saving (and hence energy savings) can be realized.

7. EFFECTS OF FLY ASH ON THE DURABILITY OF CONCRETE

"Concrete of any composition, with or without fly ash, will not deteriorate if the specifications covering its production are correctly prepared and are followed." — Bryant Mather, 1983.

Failure of concrete after a period of years less than the lifetime for which it was designed may be caused by the environment to which it has been exposed or by a variety of internal causes. External causes may be physical or chemical in nature: weathering, extremes of temperature, abrasion, or chemical action in the cement, aggregate, or reinforcement components. Internal causes may lie in the choice of materials or in inappropriate combinations of materials, and may be seen as alkali-aggregate expansion or other forms of failure. Of all the causes of lack of durability in concrete the most widespread is excessive permeability. Permeable concrete is vulnerable to attack by almost all classes of aggressive agents. To be durable, portland cement concrete must be relatively impervious.

Increasingly, concrete is being selected for use as a construction material in aggressive or potentially aggressive environments. Concrete structures have always been exposed to the action of sea water. In modern times, the demands placed on concrete in marine environments have increased greatly, as concrete structures are used in arctic, temperate, and tropical waters to contain and support the equipment, people, and products of oil and gas exploration and production. Concrete structures are used to contain nuclear reactors and must be capable of containing gases and vapours at elevated temperatures and pressures under emergency conditions. Concrete is increasingly being placed in contact with sulphate and acidic waters. In all of these instances, the use of fly ash as concrete material has a role, and an understanding of its effect on concrete durability is essential to its correct and economical application.

The following sections of this chapter seek to provide a general view of the present knowledge regarding the durability of fly ash concrete. The subject matter is vast, complex, and as yet incompletely understood. The reader desiring a more detailed treatment of the subject is recommended to consult the cited research literature for more complete discussions.

Effects of Fly Ash on Permeability of Concrete

The movement into a concrete mass of aggressive solutions or the removal of the dissolved reaction products out of concrete must play a primary role in determining the rate of progress of concrete deterioration caused by chemical attack. Permeability of a concrete mass is therefore fundamental in determining the rates of mass-transport relevant to destructive chemical action. It should be recognized that all the cementitious hydrates and some of the aggregates from which concretes are made are inherently subject to attack, not only by sulphates, chlorides, acids, and organic agents, but by water alone. That concrete survives aqueous environments at all is attributable to (a) the low equilibrium solubility of the hydrated components and (b) the low rate of mass transfer in well-compacted, cured concrete. Given any combination of cement and aggregate, it is generally observed that the less permeable the concrete, the greater will be its resistance to aggressive solutions or pure water.

A number of investigations have been made of the influence of fly ash on the relative permeability of concrete pipe containing fly ash substituted for cement in amounts of 30 and 50%. Davis (149) examined the permeability of concrete pipe incorporating fly ash substituted for cement in amounts of 30 to 50%. Permeability tests were made on 150 mm× 150 mm cylinders at ages of 28 days and 6 months (149). The results of these tests are shown in Table 7.1.

Table 7.1 — Relative permeability of concretes with and without fly ash*

Fly ash		W/(C+F)	Relative permeability	
Type	% by weight	by weight	28 days	6 months
None	—	0.75	100	26
Chicago	30	0.70	220	5
	60	0.65	1410	2
Cleveland	30	0.70	320	5
	60	0.69	1880	7

*From reference 149.

It is clear from these data that the permeability of the concrete was directly related to the quantity of hydrated cementitious material at any given time. After 28 days of curing, at which time little pozzolanic activity would have occurred, the fly ash concretes were more permeable than the control concretes. At 6 months, this was reversed. Considerable imperviousness had developed, presumably due to the pozzolanic influence of fly ash.

Kanitakis (150) used an *Initial Surface Absorption Test* to examine concrete with and without a low-calcium fly ash (CaO = 2.0%) made using the mix proportions shown in Table 7.2. Absorption measurements were made at 7, 17, 28, and 56 days of curing and the data shown in Figure 7.1 were obtained.

Table 7.2 — Mix designations and proportions for concretes examined by Kanitakis*

Mix	Constituents (per m^3)				
	Cement kg	Fly ash kg	Sand kg	Stone kg	Water L
N	400		586	1190	233
M	350	100	519	1213	227

*From reference 150.

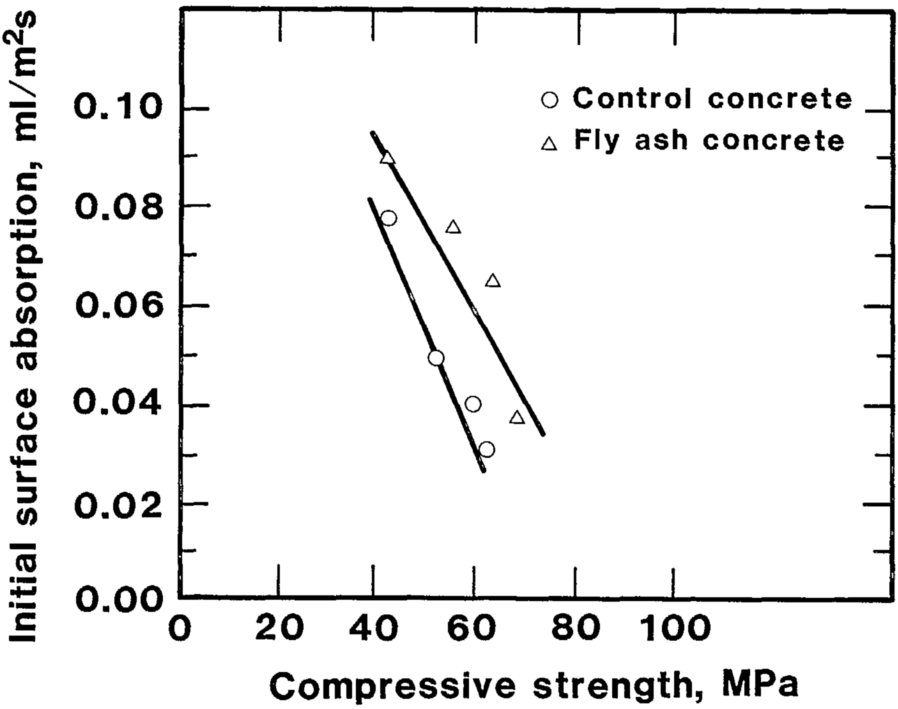

Fig. 7.1 — Initial surface absorption of water versus compressive strength of concretes (150)

The author concluded that at early ages fly ash concrete behaves as a *lean-mix* concrete and is thus permeable. At later ages, permeability is reduced as the pozzolanic action proceeds.

The rather limited observations on this very important aspect of fly ash concrete are consistent with the view expressed by Manmohan and Mehta (151) that the transformation of large pores to fine pores, as a consequence of the pozzolanic reaction between portland cement paste and fly ash, substantially reduced permeability in cementitious systems.

Diffusion of ions, such as chlorides, that are not specifically bound by the components of concrete is reasonably represented by Fick's diffusion equation (152,153):

$$\frac{dc}{dt} = D_c \cdot \frac{d^2c}{dx^2}$$

where:

C = chloride ion concentration at a distance x, after a time t;

D_c = the chloride ion diffusion coefficient.

For concrete in offshore structures, Browne (152) has reported values for D_c of 1.0×10^{-9} to 50.0×10^{-9} cm^2/s for high- and normal-strength concrete, respectively.

Short and Page (154) have reported on the diffusion of chloride ions in solution into portland and blended cement pastes and have found the following values of D_c for different cement types:

Type of cement	**$D_c \times 10^9$ (cm^2/s)**
Normal portland	44.7
Sulphate resisting	100.0
Fly ash/portland	14.7
Slag/portland	4.1

It was concluded from these data that slag and fly ash cements were more effective in limiting chloride diffusion in pastes than were normal or sulphate-resisting cements.

Permeability to gases, in particular to air and carbon dioxide, is important to some aspects of concrete durability related to carbonation (see below). Kasai et al. (155) examined the air permeability of mortars (moist cured for 1, 3, and 7 days) of blended cements made with fly ash and with blast furnace slag and concluded:

— The air permeability of blended cements is greater than that of portland cements.

— When early moist curing is extended, the permeability becomes reduced.

The considerable differences in the strengths at all ages of the mortars examined by these authors, with fly ash mortars being some 20 to 30% weaker, suggest that the curing regimes adopted were inadequate to permit any conclusions relevant to the practical behaviour of blended cement concretes in the field.

Effects of Fly Ash on Carbonation of Concrete

Calcium hydroxide and, to a lesser extent, the calcium silicates and aluminates in hydrated portland cement react in moist conditions with carbon dioxide from the atmosphere to form calcium carbonate. The process, termed carbonation, occurs in all portland cement concretes. The rate at which concrete carbonates is determined by its permeability, degree of saturation with water, and the mass of calcium hydroxide available for reaction. Well-compacted and properly cured concrete, at a low water-to-cement ratio, will be sufficiently impermeable to resist the advance of carbonation beyond the first few millimeters.

If carbonation progresses into a mass of concrete, three deleterious consequences may follow:

- Permeability may increase.
- Shrinkage may occur.
- Carbonation of the concrete immediately adjacent to steel reinforcement may reduce its resistance to corrosion.

In 1968, results from long-term investigations of concrete in Japan were reported (156,157) indicating that concrete made with blended cements was subject to more rapid carbonation than normal portland cement concrete. Other investigations (158-160) have not shown any appreciable differences in this regard, provided that the strength of the concretes being compared is equal.

In 1980, Tsukayama et al. (161) reported data from experiments conducted over a long period on fly ash concretes exposed in the field in Japan.

They found that the depth of carbonation (termed *neutralization* by the authors) was found to be related to the quality of the concrete in the following ways:

- A linear relationship was found between water-to-cement ratio (excluding fly ash) and depth of neutralization (Fig. 7.2).
- At identical water-to-cement ratios, when fly ash was added, depth of carbonation was found to be slightly decreased (see Fig. 7.2).
- The period of curing in water, after casting the specimens, was found to have a substantial influence on concrete exposed indoors. Concrete exposed outdoors was adequately cured after about one week in water (Fig. 7.3).

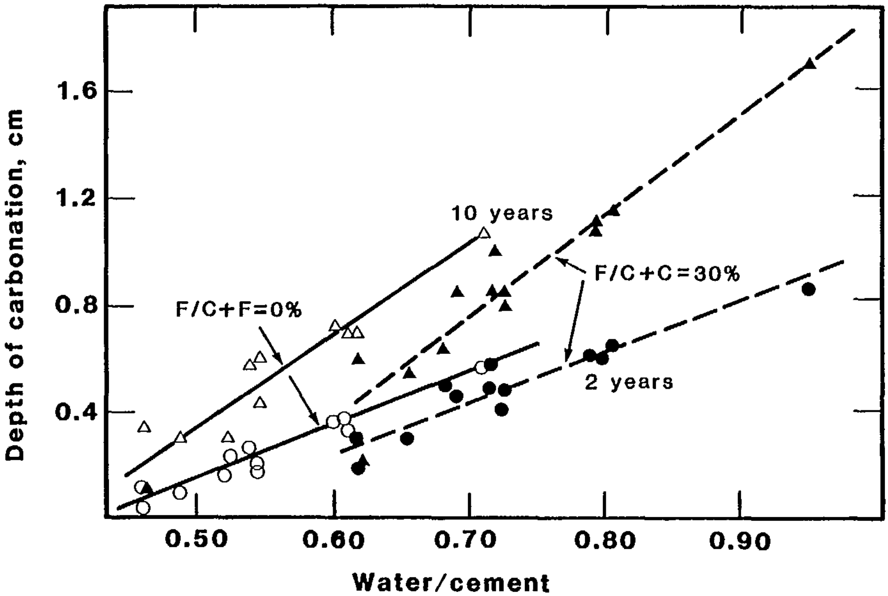

Fig. 7.2 — Depth of neutralization (carbonation) versus water/cementitious materials of concretes (161)

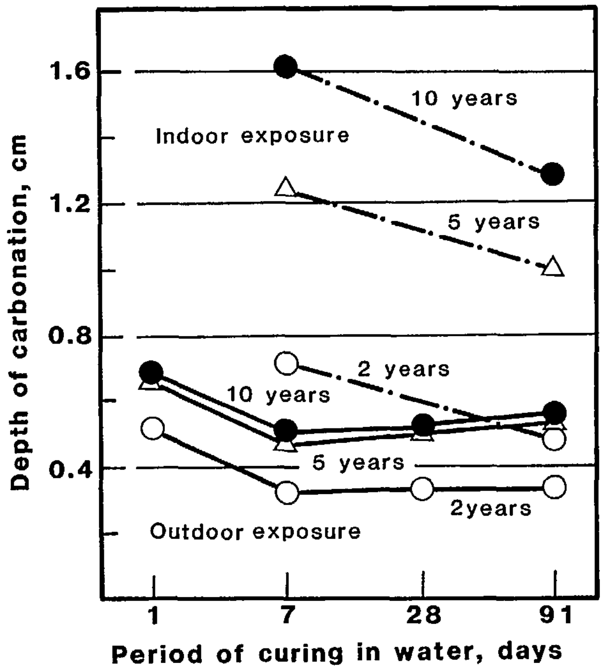

Fig. 7.3 — Depth of neutralization (carbonation) versus period of curing of fly ash concretes (161)

Gebauer (162) examined slabs of steel-reinforced concretes with the properties and mix proportions shown in Table 7.3. The slabs, 100 × 50 × 7 cm, were formed by compaction and vibration. They were cured for 7 days at 20°C and 95% R.H. Subsequently, one slab of each composition was placed in an outdoor testing station; control slabs were kept under moist curing conditions (indoor slabs). The compressive strengths of companion prisms were measured at 28 and 365 days.

Table 7.3 — Mix designations and proportions for concretes*

Mix	Cement type	Cement kg/m³	W/C	Slump cm	Compressive strength, MPa 28 days	1 year
1	Portland #1	300	0.50	3.7	36.7	47.7
2	Portland #1	300	0.55	10.5	32.8	42.3
3	Portland #1	300	0.60	16.0	28.5	38.6
4	Portland #2	300	0.50	2.7	43.2	52.9
5	Portland #2	300	0.55	8.3	37.9	48.0
6	Portland #2	300	0.60	15.0	33.8	43.6
7	Blended #1 10% ash	300	0.50	5.5	46.4	46.4
8	Blended #1 10% ash	300	0.55	13.5	42.9	42.9
9	Blended #1 10% ash	300	0.60	16.0	38.9	38.9
10	Blended #1 20% ash	300	0.50	8.0	45.2	45.2
11	Blended #1 20% ash	300	0.55	14.0	39.8	39.8
12	Blended #1 20% ash	300	0.60	20.0	35.5	35.5
13	Portland #3	350	0.47	3.8	54.8	54.8
14	Blended #3 20% ash	350	0.47	3.5	55.8	55.8
15	Portland #1	350	0.45	3.3	53.4	53.4
16	Blended #1 20% ash	350	0.43	4.0	54.8	54.8
17	Blended #1 20% ash	350	0.46	4.8	54.5	54.5

*From reference 162.

Tables 7.4 and 7.5 summarize the data from indoor and outdoor exposure, respectively.

Table 7.4 — Carbonation of concrete slabs stored indoors*

Mix	Strength MPa	Pulse velocity m/sec	Depth of carbonation mm	
			Bottom	Top
1	51.8	4983	0.5	1.0
2	51.5	4885	1.0	2.0
3	46.7	4779	1.0	2.5
4	60.5	5046	0.5	1.0
5	55.5	4970	0.5	1.0
6	50.0	4802	1.0	2.0
7	47.9	4983	1.0	1.5
8	50.3	4897	1.0	1.5
9	42.0	4756	2.0	3.0
10	41.8	4909	1.0	1.5
11	37.5	4837	2.0	2.0
12	35.9	4722	3.0	2.0
13	59.9	5020	0.5	0.5
14	51.7	4995	1.5	1.0
15	62.2	5046	0.5	0.5
16	56.5	5020	1.5	2.0
17	47.5	4958	1.5	2.5

*From reference 162.

Table 7.5 — Carbonation of concrete slabs stored outdoors*

Mix	Strength MPa	Pulse velocity m/sec	Depth of carbonation mm	
			Bottom	Top
1	62.0	4945	0.5	1.5
2	57.6	4825	1.0	3.0
3	50.6	4699	1.0	5.0
4	63.1	4921	0.5	1.0
5	61.0	4861	0.5	2.5
6	55.0	4779	1.0	3.0
7	52.7	4897	1.0	3.0
8	48.1	4707	1.0	2.5
9	40.2	4341	2.0	5.0
10	46.7	4873	1.0	5.5
11	40.2	4734	2.0	5.0
12	39.4	4623	3.0	5.5
13	63.9	4945	0.5	1.5
14	53.4	4921	1.5	2.5
15	65.4	4970	0.5	1.5
16	51.6	4995	1.5	2.5
17	51.9	4897	1.5	2.0

*From reference 162.

Gebauer reported that carbonation depth increased as:

— strength and pulse velocity decreased (regardless of composition);

— water-to-cement ratio increased;

— cement content decreased;

— fly ash content increased.

The primary correlation was found to be between carbonation depth and compressive strength (determined on cores of the slabs, not on test prisms) as is seen in Figures 7.4 and 7.5.

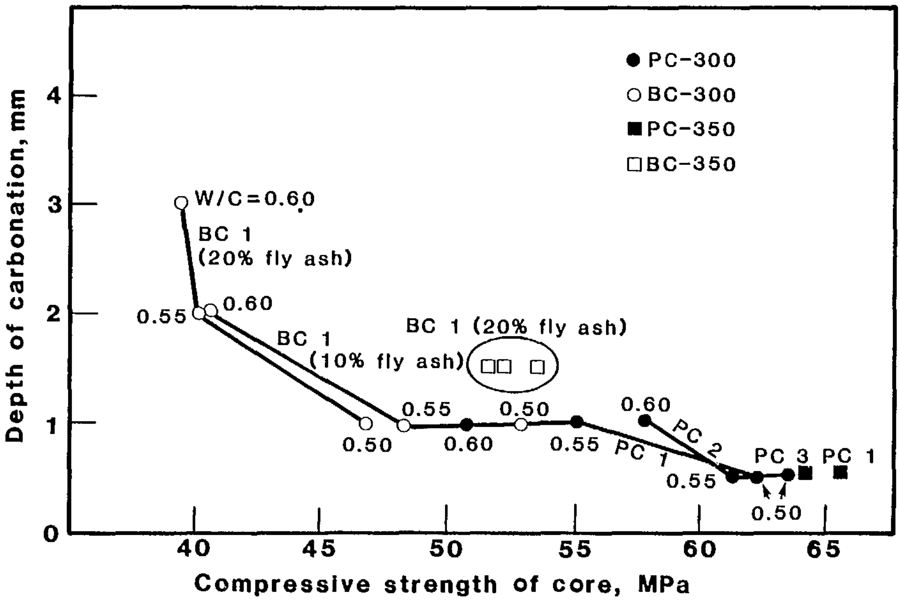

Fig. 7.4 — Depth of carbonation versus compressive strength of fly ash concretes (indoor exposure) (162)

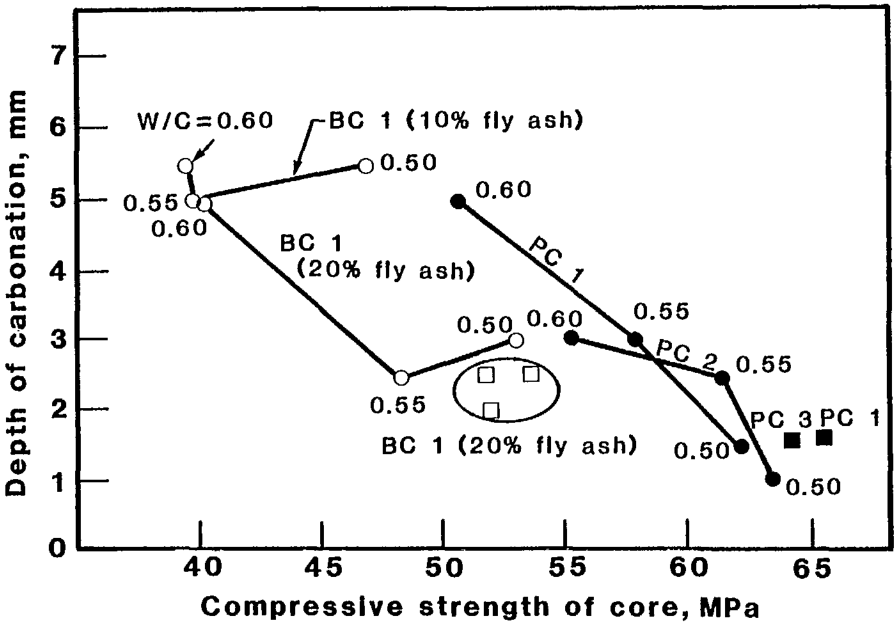

Fig. 7.5 — Depth of carbonation versus compressive strength of fly ash concretes (outdoor exposure) (162)

The rate of strength development in thin slabs was found to be different between the fly ash and control concretes. This is not unexpected because fly ash was incorporated by simple replacement. What is surprising is that strength equality was not reached even after five years with as little as 10% fly ash replacement (see Table 7.3). This suggests that a very unreactive fly ash was used.

Ho and Lewis (163) examined the rates of carbonation of three types of concrete (plain, water-reduced, and fly ash) at equal slump. Accelerated carbonation was induced by storing specimens in an enriched CO_2 atmosphere (4%) at 20°C and 50% RH for eight weeks. The authors note that one week under these conditions is approximately equivalent to one year in a normal atmosphere (0.03% CO_2).

The data from this study are presented in Figure 7.6 in terms of depth of carbonation versus 28-day compressive strength.

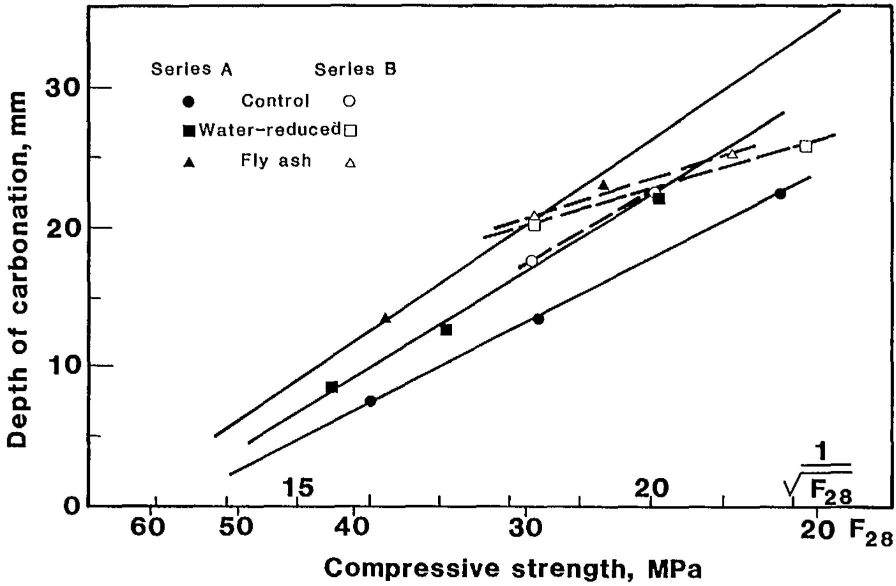

Fig. 7.6 — Depth of carbonation versus compressive strength of fly ash concretes (accelerated testing) (163)

It is clear that there is an inverse relationship between strength and depth of carbonation and that the fly ash concrete was more readily carbonated than the non-fly ash concrete, especially at lower strengths (<30 MPa).

Depth of carbonation versus cement content is shown in Figure 7.7 as a function of time of moist curing.

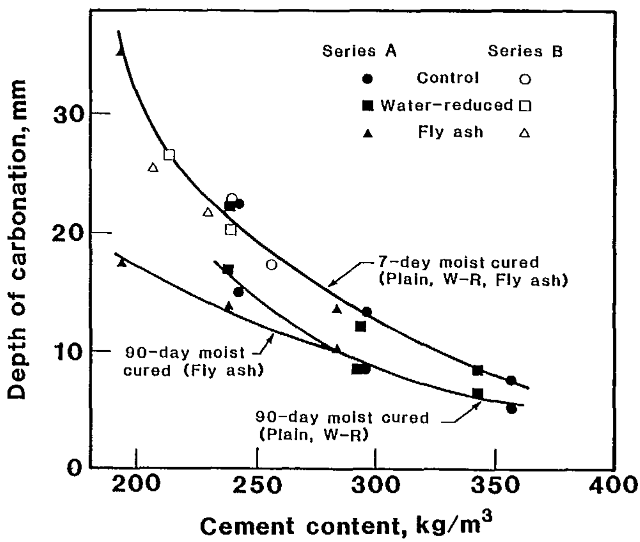

Fig. 7.7 — Depth of carbonation versus cement content of fly ash concretes (accelerated testing) (163)

The authors concluded as follows:

- — Concretes having the same strength and water-to-cement ratio do not necessarily carbonate at the same rate.
- — Based on a common 28-day strength, concrete containing fly ash showed a significant improvement in quality when curing was extended from 7 to 90 days. Such improvement was much greater than that achieved for the plain concrete.
- — The depth of carbonation is a function of the cement content for concretes moist-cured for 7 days. However, with a further curing to 90 days, concrete containing fly ash showed a slower rate of carbonation as compared to plain and water-reduced concretes.

There is no doubt that these conclusions are consistent with the reported observations. However, the approach taken in this research has a major weakness, the influence of which must not be disregarded. In the accelerated test, concrete specimens that have been moist-cured for 7 days, conditioned in the laboratory for 21 days at 20°C and 50% RH, are exposed to CO_2 (at elevated pressure) for eight weeks. The age of the concrete at the start of the test is 28 days. Its maturity, however, is considerably less than an equivalent 28-day moist-cured concrete (although it is arguable that it is closer to the condition of *real* concrete in most construction situations). The concrete is exposed to a rate of carbonation at least five times that of atmospheric exposure while at the same time being kept at 50% RH (163). The disparity between the rate of carbonation and the rate of maturing is extreme and becomes greater the longer the experiment proceeds.

As Buttler et al. (164) have noted, the accelerated test may be capable of application to different cements with different mix proportions. It is not applicable when comparing concretes made with portland cement with those made with blended cements because of the slow rate of pozzolanic reactions.

In general, it appears that good-quality fly ash concrete is comparable to plain concrete in its resistance to carbonation. If concrete is placed at a low cement factor, with insufficient curing (either lack of moisture or low temperature), it should come as no surprise to find that it is not durable to all forms of chemical and physical aggression, including carbonation.

Effects of Fly Ash on the Durability of Concrete to Repeated Cycles of Freezing and Thawing

It is now generally accepted, other criteria also being met, that air-entrainment renders concrete frost-resistant. As was discussed in Chapter 3, fly ashes, in common with other finely divided mineral components in concrete, tend to cause an increase in the quantity of admixture required to obtain specified levels of entrained air in concrete. In some instances, the stability or rate of air loss from fresh concrete is also affected. In general, the observed effects of fly ash on freezing and thawing durability support the view expressed by Larson (69):

> "... Fly ash has no apparent ill effects on the air voids in hardened concrete. When a proper volume of air is entrained characteristics of the void system meet generally accepted criteria."

Gebler and Klieger (76) extended their study of air-entrainment of fly ash concrete (see Chapter 3) to include an examination of the air-void parameters of hardened concretes cast after initial mixing, and after 30, 60, and 90 minutes. From these experiments the authors concluded as follows:

> "Spacing factors ($\bar{L}$) of specimens cast over a period of 90 minutes were essentially constant for the majority of concretes containing fly ash. In addition, the initial spread of results of specific surface and voids per inch was essentially similar for concretes containing Class F or Class C ash. However, when measured on specimens cast at 90 min., concretes with Class F ash exhibited greater variability of results for these air-void parameters than concretes with Class C ash."

Sturrup, Hooton, and Clendenning (165), related the freezing and thawing performance of low-calcium fly ash concretes to carbon content. Accelerated freezing and thawing tests (ASTM C 666, Procedure A) and outdoor exposure tests were conducted on concrete specimens containing low-calcium ashes of 5.4, 12.3, and 23% carbon, at 15, 30, 45, and 60% replacement of cement by weight. Water-to-cement-plus-fly ash ratios were kept constant at 0.6 and with the exception of a specimen at 23% carbon (air content = 3.6%) air content was kept at 6.5 ± 1%.

It was reported that correlation between durability factor, as determined by resonant frequency, and carbon content was poor; correlation with weight loss resulting from freezing and thawing cycling was more definite. This was taken to indicate that surface scaling, rather than internal damage, was the result of frost action on the specimens (166). This was confirmed by observation of outdoor exposed specimens (167).

Yuan and Cook (83) have reported on the freezing and thawing resistance of concrete incorporating high-calcium fly ash. Two series of concrete specimens (non-air-entrained, air-entrained) were examined with 0, 20, 30, and 50% replacement of cement by weight. The freezing and thawing durability, as determined by relative dynamic modulus, is shown in Figures 7.8 and 7.9 and by weight loss for air-entrained concrete in Figure 7.10. Yuan and Cook made the following observations:

— The superior freezing and thawing resistance of air-entrained concrete is evident with or without fly ash replacement.

— The concrete with 20% of fly ash was found to be more durable than the control.

— As the quantity of fly ash in air-entrained concrete was increased to 50%, more scaling damage was noted after 400 cycles.

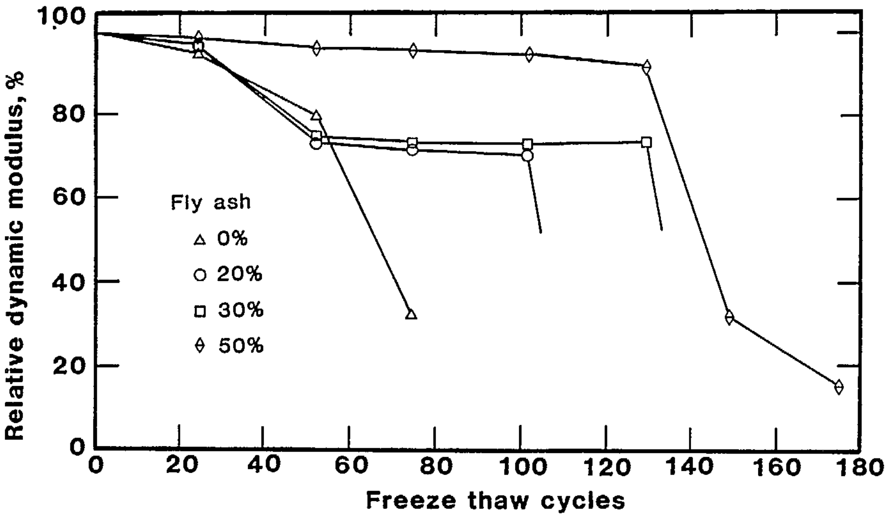

Fig. 7.8 — Relative dynamic modulus versus number of freeze-thaw cycles for non-air-entrained fly ash concretes after 14 days of curing (83)

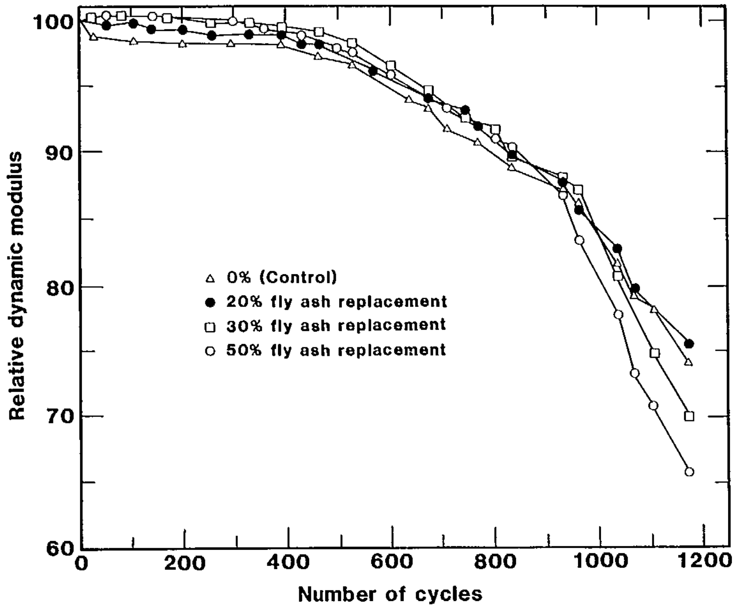

Fig. 7.9 — Relative dynamic modulus versus number of freeze-thaw cycles for air-entrained fly ash concretes after 14 days of curing (83)

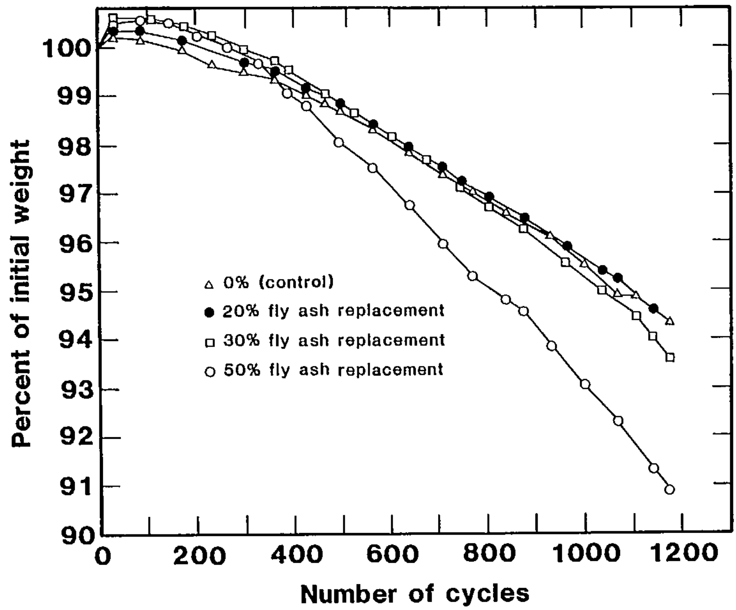

Fig. 7.10 — Weight loss versus number of freeze-thaw cycles for air-entrained fly ash concretes after 14 days of curing (83)

Ramakrishnan et al. (43) also examined the freezing and thawing durability of concrete containing a high-calcium fly ash (CaO = 20.1%). Their data for concretes with Type III cement are shown in Figures 7.11 and 7.12. Similar weight change, pulse velocity development and dynamic modulus data were found for concretes with and without fly ash.

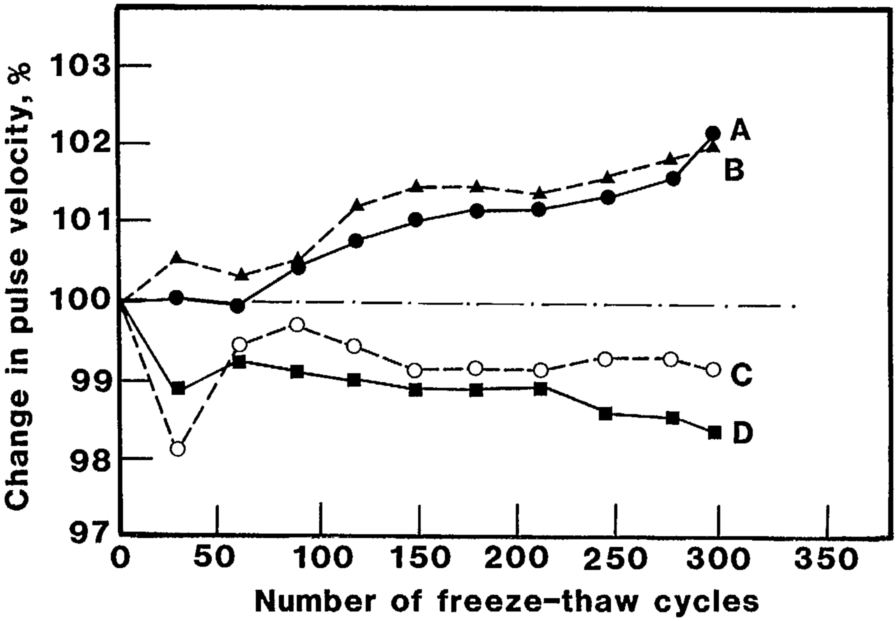

Fig. 7.11 — Pulse velocity changes of fly ash concretes under rapid freeze-thaw cycling (43)

Key: A — Control mix; Standard moist cure
B — Fly ash mix; Standard moist cure
C — Fly ash mix; Freeze-thaw cure
D — Control mix; Freeze-thaw cure

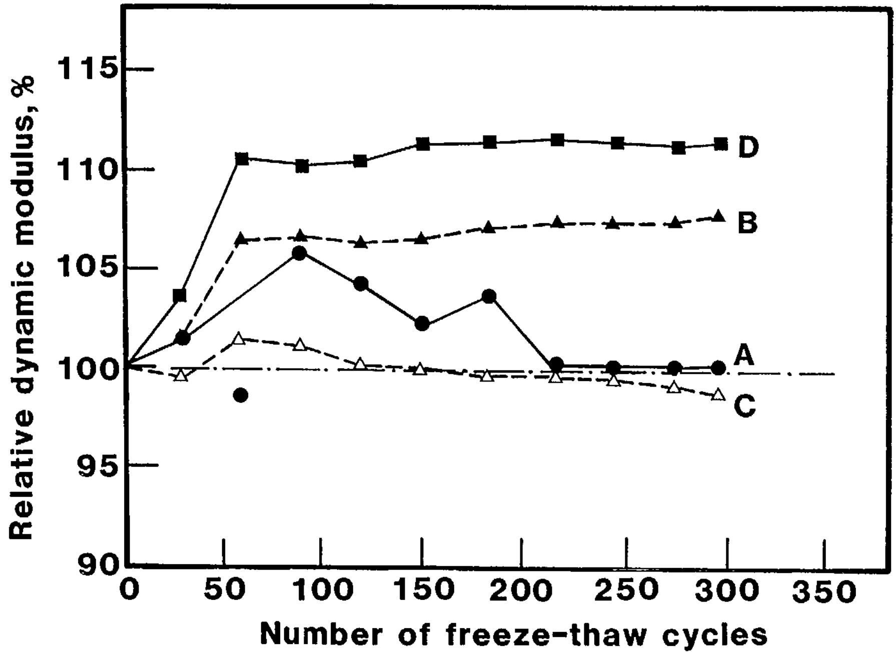

Fig. 7.12 — Relative dynamic modulus changes of fly ash concretes under rapid freeze-thaw cycling (43)

Key: A — Control mix; Freeze-thaw cure
B — Fly ash mix; Standard moist cure
C — Fly ash mix; Freeze-thaw cure
D — Control mix; Standard moist cure

The freezing and thawing resistance of fly ash concretes incorporating both low- and high-calcium fly ashes was determined in the CANMET study (38). Table 7.6 shows the durability factors found for specimens made from the concretes described elsewhere in this report (see Tables 3.2 and 4.1, Chapters 3 and 4, respectively).

Table 7.6 — Freeze-thaw durability factors for fly ash concretes*

Mixture No.	Air content %	Durability factor after 300 cycles, %**
Control 1	6.5	97.7
Control 2	6.4	98.1
F1	6.2	96.4
F2	6.2	98.8
F3	6.2	96.8
F4	6.3	98.8
F5	6.4	97.2
F6	6.5	96.8
F7	6.1	97.6
F8	6.2	96.9
F9	6.4	97.6
F10	6.5	97.2
F11	6.6	95.8

*From reference 38.
**Determined in accordance with ASTM C-666.

Virtanen (81) compared the freezing and thawing resistance of fly ash, condensed silica fume, and slag concretes. The observations made in this work with regard to AEA demand were discussed in Chapter 3. An estimate was made of the relative *theoretical service life* for each type of concrete as a function of air content (Fig. 7.13) and the author made the following observations:

— "The air content has the greatest influence on the freeze–thaw resistance of concrete.

— "Addition of fly ash has no major effect on the freeze–thaw resistance of concrete if the strength and air content are kept constant.

— "The addition of blast-furnace slag or fly ash may have a negative effect on the freeze–thaw resistance of concrete when a major part of the cement is replaced by them."

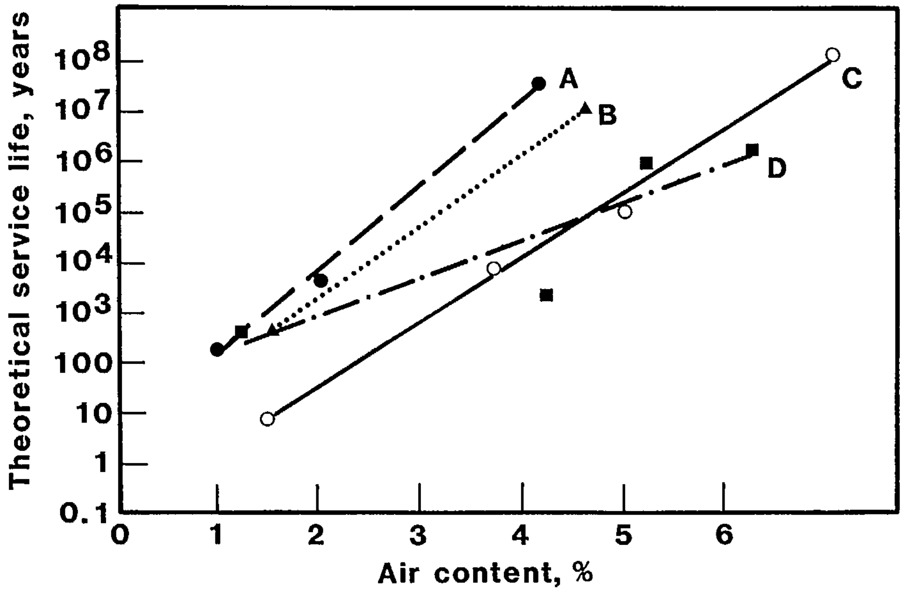

Fig. 7.13 — Relationship between theoretical service life and air content of fresh concrete (81)

***Key:** A — Concretes incorporating ground, granulated blast-furnace slag*
B — Concretes incorporating condensed silica fume
C — Control concretes
D — Concretes incorporating fly ash

Larson (69), discussing some of the difficulties of interpreting the findings of much of the early work on freezing and thawing resistance of fly ash concrete, made the following observation:

> "Fly ash concrete durability characteristics are influenced and obscured by all the factors operating on ordinary concrete. They are also related to variations in the fly ash itself and perhaps to the associated phenomenon of increased air-entraining-agent requirement. When valid comparisons are made with equal strengths and air contents, however, there are no apparent differences in the freezing and thawing durability of fly-ash and non fly-ash concretes."

In relation to testing methodology, it has been noted by Elfert (62) that the type of curing of specimens used to evaluate freezing and thawing resistance greatly influences the results obtained with fly ash and pozzolan concretes. Figure 7.14 illustrates the differences obtained under moist-curing and simulated field conditions.

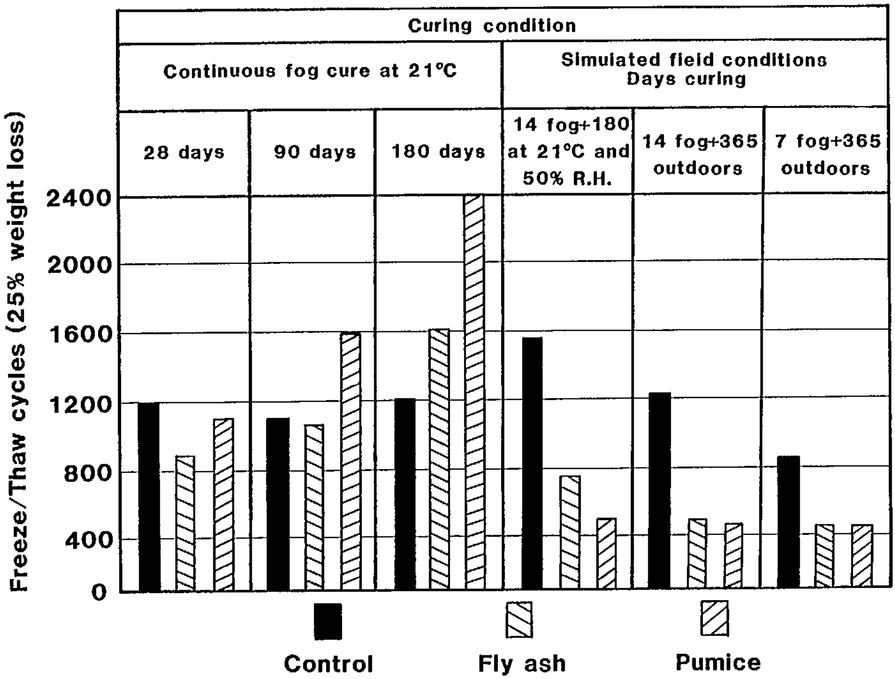

Fig. 7.14 — The effect of curing conditions on freeze-thaw durability of concrete containing pozzolan (62)

Another aspect of freezing and thawing testing procedure has been criticized by Brown et al. (168) who made the following comments on freezing and thawing testing of blended cements:

— "When blended cements are tested according to ASTM C 666-73, the standard method for measuring the freezing and thawing durability of portland cement concretes, inferior resistance is usually observed. This is probably because test initiation after only a short curing period does not make proper allowance for the generally lower rate of strength development of blended cements.

— "Freezing and thawing studies, when initiated after longer curing periods, have indicated that blended cements, due to development of strengths equivalent or superior to those of portland cements, also develop superior resistance to freezing and thawing."

These points should certainly be kept in mind when consideration is being given to reports of all aspects of the durability of fly ash concrete, not merely to its frost resistance.

Effects of Fly Ash on Durability of Concrete Exposed to Elevated Temperatures

The influence of elevated temperatures on the strength of concrete during curing has been discussed at some length in Chapter 4 of this report. In recent years, the use of concrete in structures required to withstand elevated temperatures under some circumstances (such as nuclear reactor containment structures) has generated renewed interest in the effects of high temperatures on fly ash and other concretes.

Nasser and Lhotia (169,170) and Nasser and Marzouk (103,171) have studied plain and fly ash concretes at temperatures up to 230°C. Carette, Painter, and Malhotra (172) have studied concretes with normal portland cement, slag, and fly ash at sustained temperatures up to 600°C. Data from this research are shown in Figure 7.15. In general, the incorporation of fly ash appears not to influence the behaviour of concrete at elevated temperatures. Loss of strength and changes in other structural properties occur at approximately the same temperatures for both types of concrete.

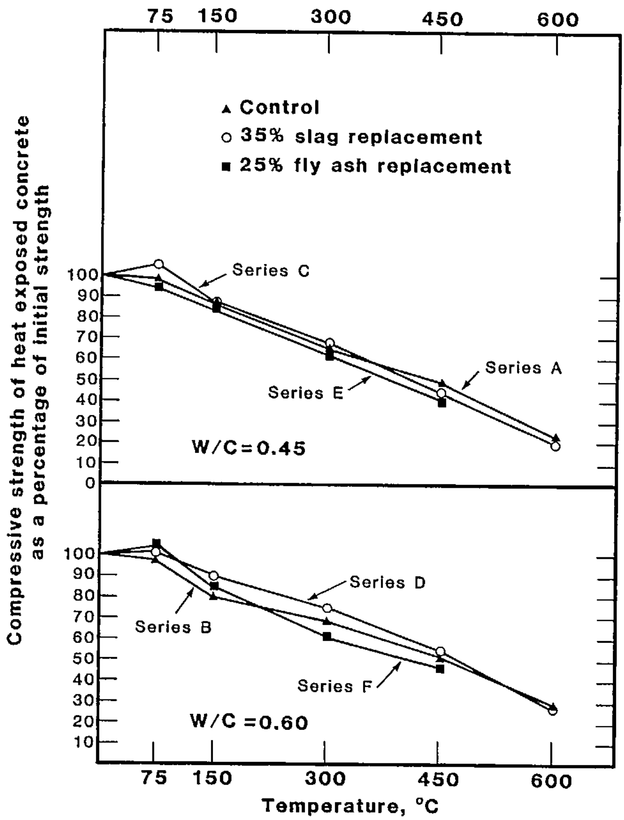

Fig. 7.15 — Compressive strength of concretes after one month of exposure to various elevated temperatures (172)

Abrasion and Erosion of Fly Ash Concrete

Under many circumstances, concrete is subjected to wear by attrition, scraping, or the sliding action of vehicles and other objects. When water flows over concrete surfaces, erosion may occur. In general, regardless of the type of test performed, the abrasion resistance of concrete is usually found to be proportional to its compressive strength (94). Similarly, at constant slump, resistance to erosion improves with increased cement content and strength. It may be anticipated that fly ash concrete that is incompletely or inadequately cured may show reduced resistance to abrasion.

Abdun-Nur cites three publications (16) indicating that abrasion resistance may be reduced in fly ash concrete. However, in none of these is there any indication that attempts were made to compare fly ash concrete and plain concrete at equal strength or equal maturity.

Liu (173) has examined the abrasion-erosion resistance of concrete using a newly developed underwater abrasion test. One of the concrete mixes examined by Liu incorporated fly ash at a 25% by volume replacement for portland cement. Details of the type and origin of the fly ash used were not reported. Performance of the fly ash concrete, cured for 90 days to an average compressive strength of 49 MPa (7170 psi), was compared with a concrete of similar mix proportions, containing no fly ash, cured for 28 days, with an average compressive strength of 47 MPa (6870 psi).

Little difference in abrasion resistance was found between the two concretes for test periods up to 36 hours. At prolonged test times, the performance of the fly ash concrete was inferior to that of the control. After 72 hours, the fly ash concrete had lost almost 25% more mass (7.6% loss) due to abrasion-erosion than the control (6.1% loss).

Presently, insufficient information is available to establish any relationship between abrasion and fly ash use, beyond that of the influence of fly ash on strength development in concretes. The resistance of fly ash concretes to erosion and abrasion under many forms of exposure urgently requires research.

Effects of Fly Ash on Durability of Concrete Exposed to Chemical Attack

Introducing fly ash as a component of concrete has been shown to influence its durability to chemical attack. Leaching of calcium hydroxide, acidic dissolution of cementitious hydrates, the action of atmospheric and dissolved carbon dioxide, and the reactivity of cement components to ions in solution are the main causes of deterioration of concrete exposed to chemical action.

Biczok (174) enumerates four conditions related to concrete quality and the constituents of concrete upon which the destructive effects of aggressive waters depend:

- — type of cement used, its chemical and physical properties;
- — quality of concrete aggregates, their physical properties and gradation;
- — method used for preparing concrete, the water-cement ratio, the proportion of cement, the placement;
- — condition of the surface exposed to the water.

Of these, condition 1 relates strictly to the nature of the cementitious binder used, whereas conditions 2, 3, and 4 may be grouped under one or more aspects of the permeability of concrete.

With regard to cement type, two factors are influential in determining the relative durability of fly ash concrete:

- — The chemical composition of the cement, vis-à-vis the cementitious components produced during hydration, has a pronounced influence on the durability with respect to chemical action. The most notable example is the use of low-C_3A, (ASTM Type V) cements as a means of controlling attack due to sulphate ions.
- — A combination of chemical composition and physical properties, notably fineness, determines the rate at which cement hydration proceeds and, at least for the early life of a structure, must influence its permeability.

Fly ash, used as a replacement for portland cement, has an indirect influence on both factors. At early ages, it serves only as an inert component and is therefore similar to reduction in cement content. At later ages, it contributes to the formation of cementitious components but, as Kovacs (175) has shown, it does so in a manner that changes the relative proportions of the usual hydrate materials. Finally, it converts some of the calcium hydroxide, which is produced when cement hydrates, to less reactive calcium silicates and aluminates, through the pozzolanic reaction. The removal of free calcium hydroxide by reactive combination with pozzolans was shown by Lea (176) to progress as is illustrated in Figure 7.16, in which the quantity of free $Ca(OH)_2$ in mortars made with and without pozzolan is compared as a function of age. It is generally considered that in concrete this process leads to long-term gains in watertightness, strength, and resistance to aggressive environments.

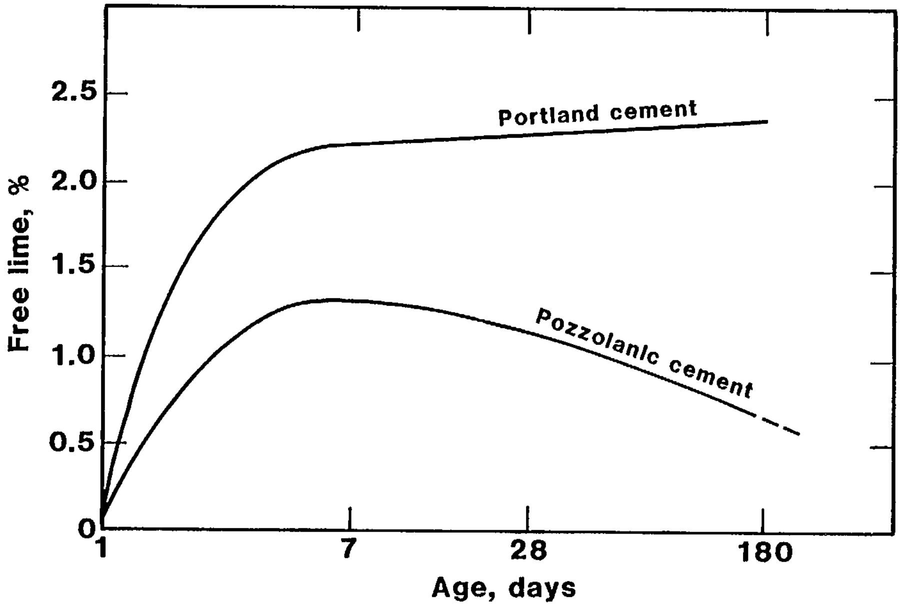

Fig. 7.16 — Free lime content of 1:3 cement sand mortars (176)

Except for general recognition of this final point, there seems to have been little consideration given in the research literature to the role played by fly ash in changing the chemical balance of the cementitious components of concrete, either as a factor in concrete durability or in respect to the development of test methods.

Effects of Fly Ash on Sulphate Resistance of Concrete

In 1937, Davis et al. (2), reported that some fly ashes increased the resistance of concrete to sulphate attack, others were ineffective, and some were deleterious and caused increased sulphate deterioration.

In 1967, Dikeou (177) reported the results of sulphate resistance studies on a total of 30 concrete mixes made from 3 portland cements, 3 portland–fly ash cements, and 12 fly ashes. From this work it was concluded that all of the fly ashes tested greatly improved sulphate resistance. The relative order of improvement found in this work is shown in Figure 7.17.

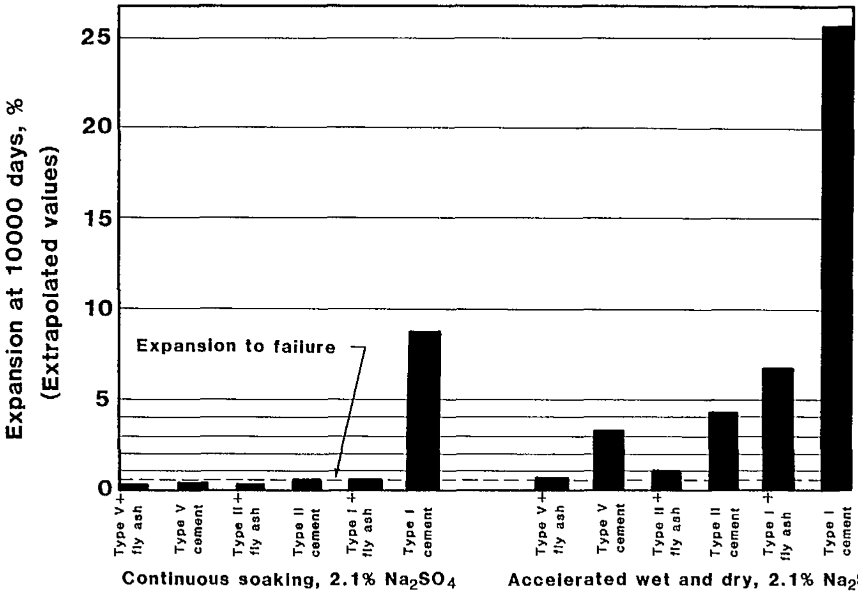

Fig. 7.17 — Sulphate expansion of concretes containing 30% of fly ash (62)

Kalousek, Porter, and Benton (178) reported studies on the requirements of concrete for long-term service when exposed to sulphate. From this work they concluded that:

— Eighty-four per cent of the ASTM Types V and II cement concretes without pozzolan showed a life expectancy of less than 50 years.

— Certain pozzolans increased very significantly the life expectancy of concrete exposed to 2.1 per cent sodium sulphate solution. Fly ashes meeting present-day specifications were prominent among the group of pozzolans showing the largest improvements.

— Concretes for long-term survival in a sulphate environment should be made with high-quality pozzolans and a sulphate-resisting cement. The pozzolan should not increase significantly, but preferably decrease, the amount of water required.

— Cement to be used in making sulphate-resisting concrete with pozzolan of proven performance should have a maximum C_3A content of 6.5 per cent and maximum C_4AF content of 12 per cent. Restrictions of cements to those meeting present-day specifications for Type V cement does not appear justified.

The fly ash samples examined by Dikeou (177) and those examined by Kalousek et al. (178) all originated from bituminous coals.

In 1976, Dunstan (179) reported the results of experiments on a total of 13 concrete mixes made using fly ashes from lignite or subbituminous coal sources. On the basis of this work he concluded that lignite and subbituminous fly ash concrete generally exhibited reduced resistance to sulphate attack.

Dunstan's work was extended and in 1980 a report (180) was published summarizing the results of a five-year study on sulphate attack on fly ash concretes. This report includes a theoretical analysis of sulphate attack and its causes. The basic postulate of Dunstan's thesis is that CaO and Fe_2O_3 in fly ash are the main contributors to the resistance or susceptibility of fly ash concrete to sulphates. Dunstan notes that as the calcium oxide content of ash increases above a lower limit of 5%, or as the ferric oxide content decreases, sulphate resistance is reduced. To use this observation as a means to select potentially sulphate-resistant fly ashes (or more importantly fly ashes that can improve the sulphate resistance of concrete), Dunstan proposed the use of a resistance factor (R) calculated as follows:

$$R = (C-5)/F$$

where:

C = per cent CaO
F = per cent Fe_2O_3.

Figures 7.18 and 7.19 show the results from two types of laboratory sulphate-resistance tests on samples of concretes containing high-calcium fly ashes with the properties shown in Table 7.7. Figures 7.20 and 7.21 show the results from similar tests on samples of concretes containing low-calcium fly ashes with the properties also shown in Table 7.7. The influences (positive and negative) of fly ash are clearly seen from these data.

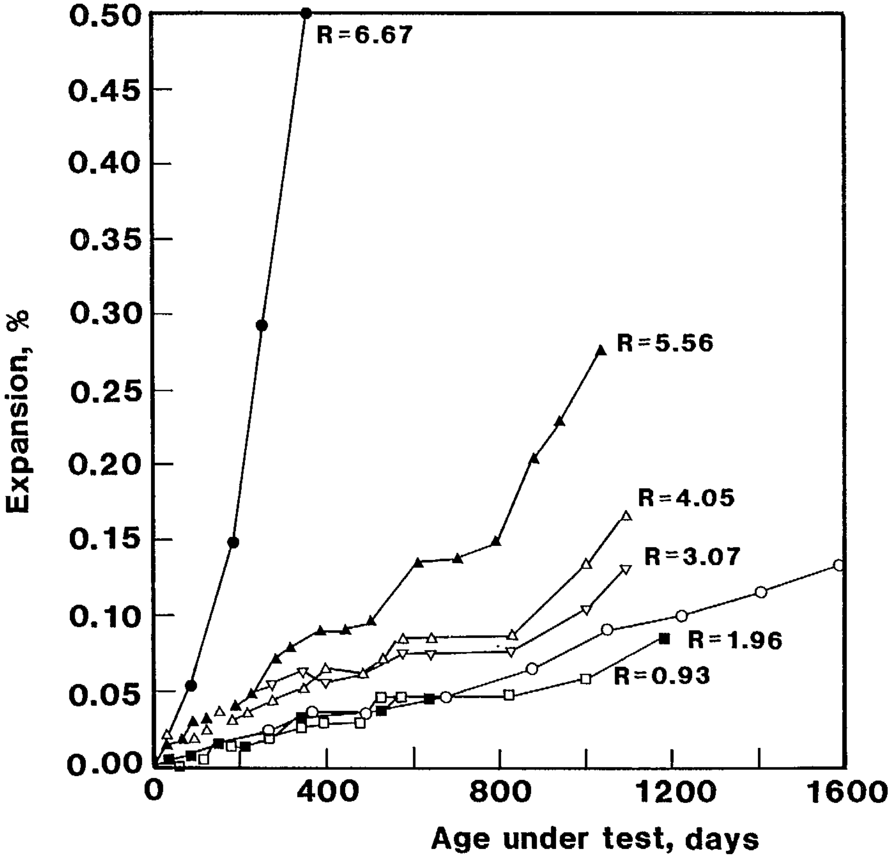

Fig. 7.18 — Sulphate expansion of concretes containing high-calcium fly ash (soak test) (180)

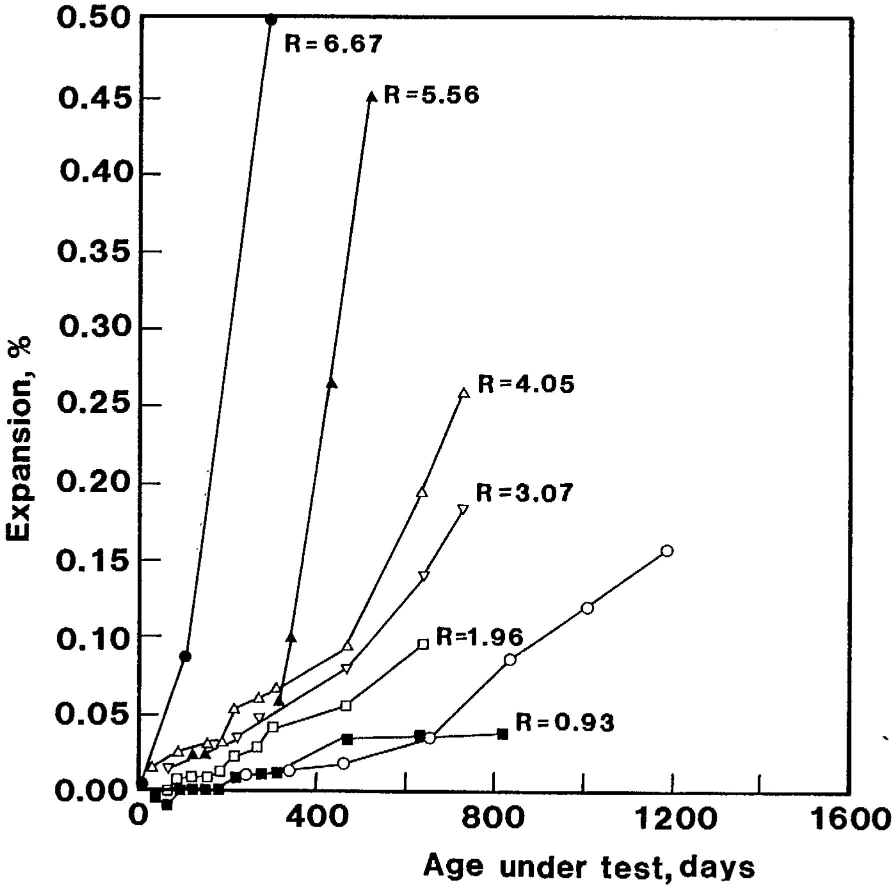

Fig. 7.19 — Sulphate expansion of concretes containing high-calcium fly ash (wet/dry test) (180)

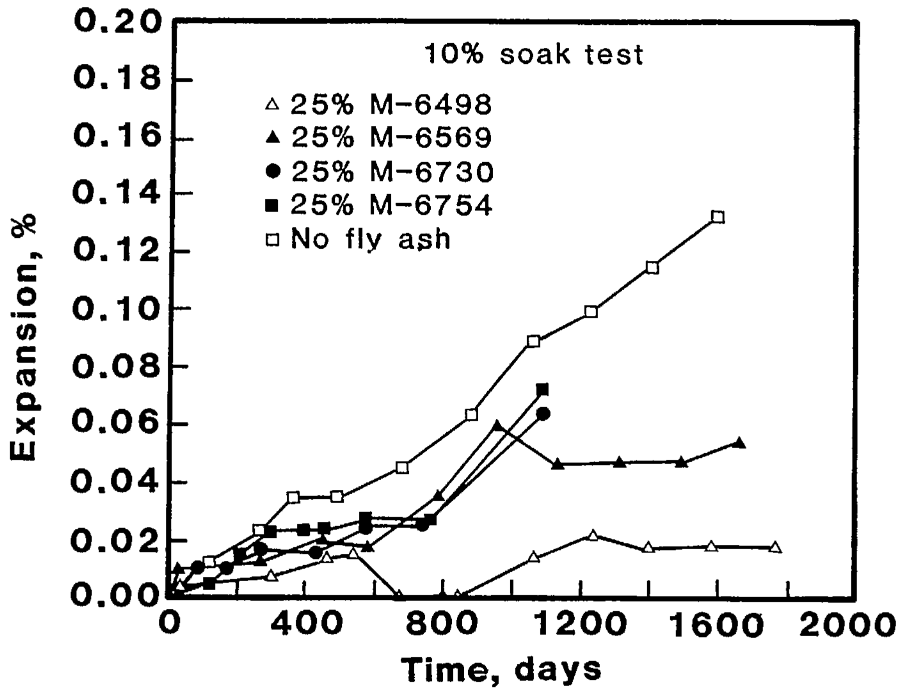

Fig. 7.20 — Sulphate expansion of concretes containing low-calcium fly ash (soak test) (179)

Table 7.7 — Characteristics of fly ashes examined by Dunstan*

	Composition, mass %							
Fly ash #	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Alkali	LOI
M-6498	46.1	19.0	18.6	8.2	1.3	1.6	0.72	2.0
M-6535	28.1	20.0	4.1	32.0	6.4	3.8	0.68	0.2
M-6734	34.7	24.8	4.2	26.1	5.2	1.4	0.81	0.2
M-6514	37.2	15.6	5.6	24.3	11.3	0.9	0.07	0.3
M-6510	37.1	11.8	7.3	21.8	5.6	2.6	4.23	0.3
M-6577	31.1	17.1	7.9	25.3	8.1	3.3	1.35	1.1
M-6569	51.8	27.2	2.0	10.7	2.1	0.7	0.86	1.2
M-6730	49.6	25.7	3.0	11.3	2.1	0.7	1.20	1.3
M-6754	61.4	23.4	3.7	7.0	1.2	0.5	0.81	2.5
M-6679	32.8	19.6	4.1	28.0	5.5	3.4	1.54	0.5
M-6680	36.9	18.1	4.7	24.0	4.8	2.8	1.86	0.6
M-6681	41.1	17.9	4.9	20.2	4.4	2.2	2.21	0.8
M-6682	45.7	18.4	5.3	15.5	3.8	1.6	2.83	0.9
M-6683	51.5	24.5	5.7	10.2	2.1	0.9	0.96	1.2
M-6734	34.7	24.8	4.2	26.1	5.2	1.4	0.81	0.2

*From references 66, 180.

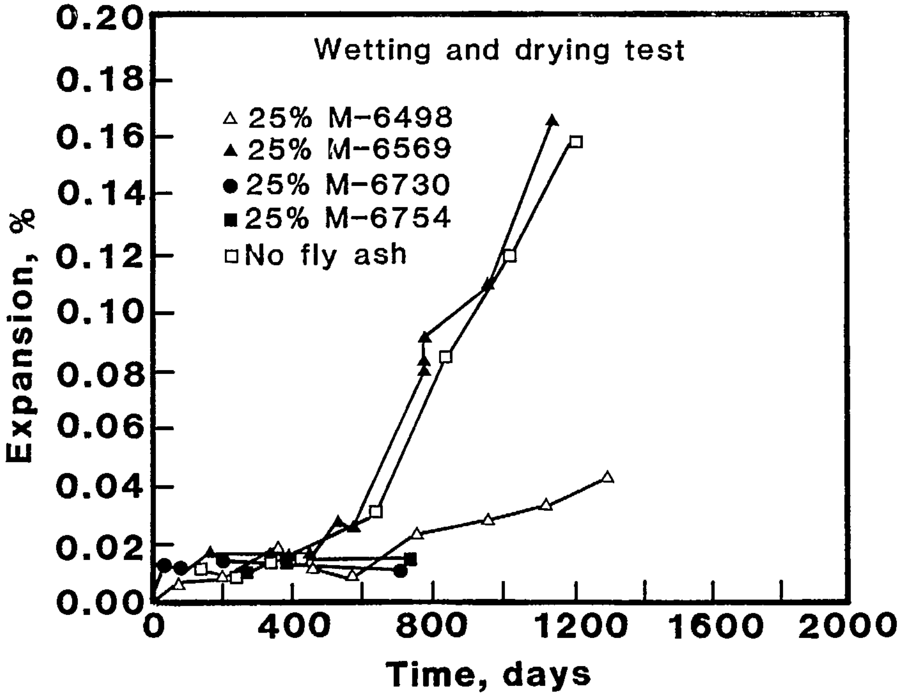

Fig. 7.21 — Sulphate expansion of concretes containing low-calcium fly ash (wet/dry test) (179)

The findings of Dunstan's work have been summarized in terms of the selection of fly ashes for sulphate-resistant concrete as follows:

R Limits*	Sulphate Resistance**
< 0.75	Greatly improved
0.75 to 1.5	Moderately improved
1.5 to 3.0	No significant change
>3.0	Reduced

The U.S. Bureau of Reclamation has incorporated a more conservative (181) version of Dunstan's limits into a recently revised reprint of the *Concrete Manual* (182), details of which are given in Table 7.8.

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*At 25% cement replacement.

**Relative to ASTM Type II cement at 0.45 w/c.

Table 7.8 — Bureau of Reclamation cementitious materials options for sulphate resistance*

I. Positive Sulphate Attack (0.10-0.2% or 150-1500 ppm)
   - A. Type II cement
   - B. Type II cement plus class N,F, or C pozzolan with R less than 2.5
   - C. Type IP (MS) cement with R less than 2.5

II. Severe Sulphate Attack (0.2-2% or 1500-10,000 ppm)
   - A. Type V cement
   - B. Type V cement plus class N,F, or C pozzolan with R less than 2.5
   - C. Type II cement plus class N,F, or C pozzolan with R less than 2.5
   - D. Type IP (MS) cement
     with R less than 2.5 if C_3A less than 5.0
     with R less than 1.5 if C_3A between 5.0 and 8.0

III. Very Severe Sulphate Attack (2% or more or >10,000 ppm)
   - A. Type V cement plus class N,F, or C pozzolan with R less than 1.5
   - B. Type II cement plus class N,F, or C pozzolan with R less than 0.75
   - D. Type IP (MS) cement
     with R less than 1.5 if C_3A less than 5.0
     with R less than 0.75 if C_3A between 5.0 and 8.0

*From reference 181.

Mather (183) has reported data from two studies in progress at the laboratories of the U.S. Corps of Engineers in which various pozzolans are under investigation for their influence on sulphate resistance of concrete. The data presented were obtained from exposure of mortars to 0.352 molar Na_2SO_4 solution. Care was taken in the experiments to expose the mortar bars to sulphate solutions only after they had reached approximately equal maturity, as determined by measurements of compressive strength on companion mortar cubes.

Three non-sulphate-resisting cements were used, with C_3A contents of 14.6% (cement RC-756), 13.1% (cement RC-714), and 9.4% (cement RC-744), respectively. Ten pozzolans were examined, comprising one condensed silica fume, one volcanic glass, three fly ashes of subbituminous origin, one bituminous fly ash, and four fly ashes from lignite coals. It is unfortunate that the chemical and physical properties of these materials are not recorded in this preliminary report of the study.

The pozzolans were incorporated in mortars by replacement of 30% (by volume) of portland cement.

Figures 7.22 to 7.25 show the results obtained from these experiments. The ranking of effectiveness in reducing sulphate expansion was found to be, from best to worst, as follows: condensed silica fume, volcanic glass, sub-bituminous fly ash (three examples), bituminous fly ash, and lignite fly ash (four examples).

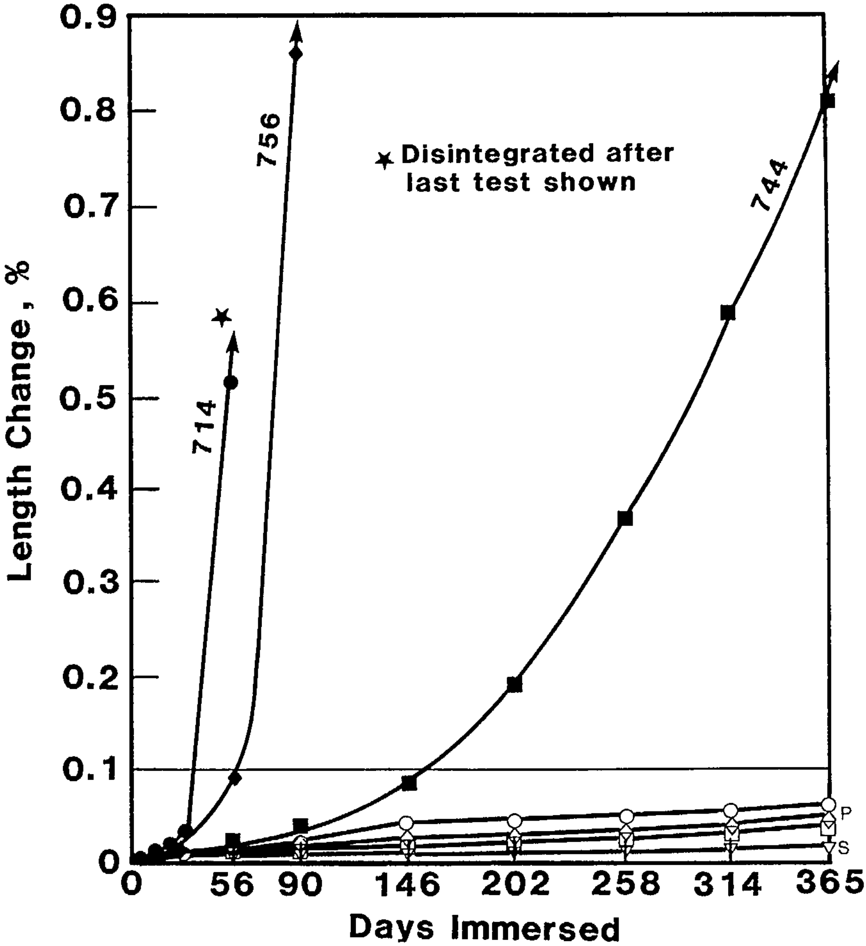

Fig. 7.22 — Effects of condensed silica fume and volcanic glass pozzolan on expansion of mortar prisms incorporating non-sulphate-resisting cement in sulphate solution (183)

Key: 714 = Cement with calculated C_3A, 13.1%
756 = Cement with calculated C_3A, 14.6%
744 = Cement with calculated C_3A, 9.4%
S = 30% replacement of cement by condensed silica fume.
P = replacement of cement by pozzolan.

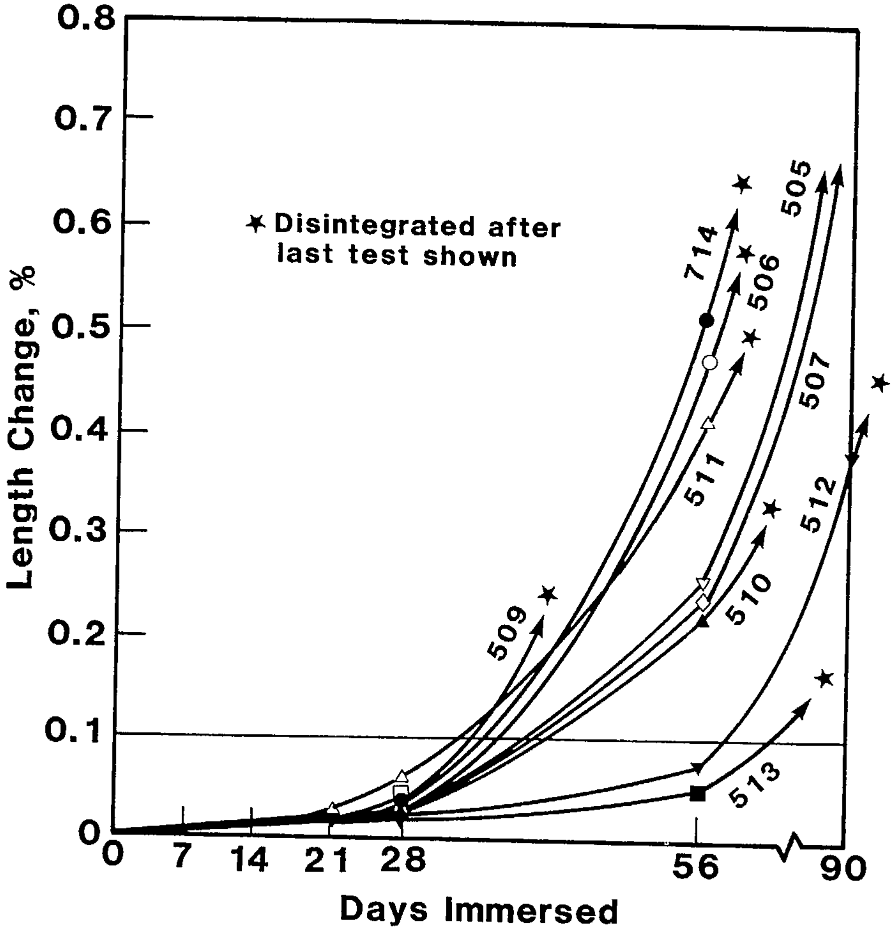

Fig. 7.23 — Effects of fly ash on expansion of mortar prisms incorporating non-sulphate-resisting cement in sulphate solution (183)

Key: 714 = Cement with calculated C_3A, 13.1%

Remaining numerals indicate replacement of cement 714 by 30% of eight different, but unidentified, fly ashes.

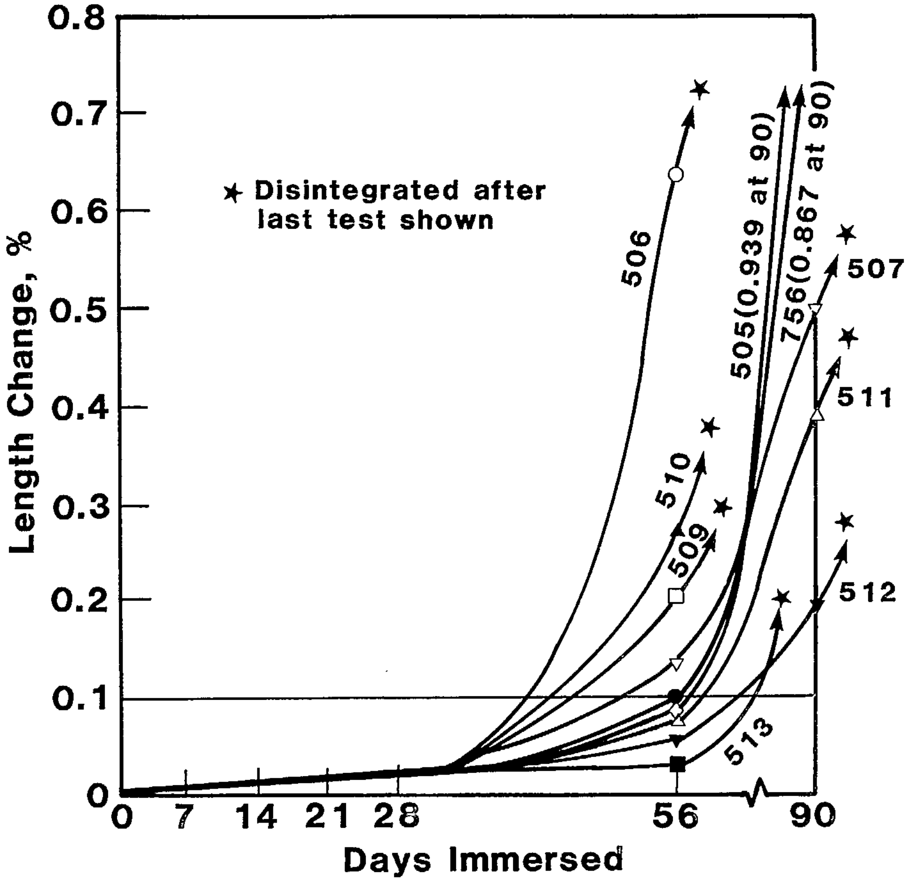

Fig. 7.24 — Effects of fly ash on expansion of mortar prisms incorporating non-sulphate-resisting cement in sulphate solution (183)

Key: 756 = Cement with calculated C_3A, 14.6%

Remaining numerals indicate replacement of cement 756 by 30% of eight different, but unidentified, fly ashes.

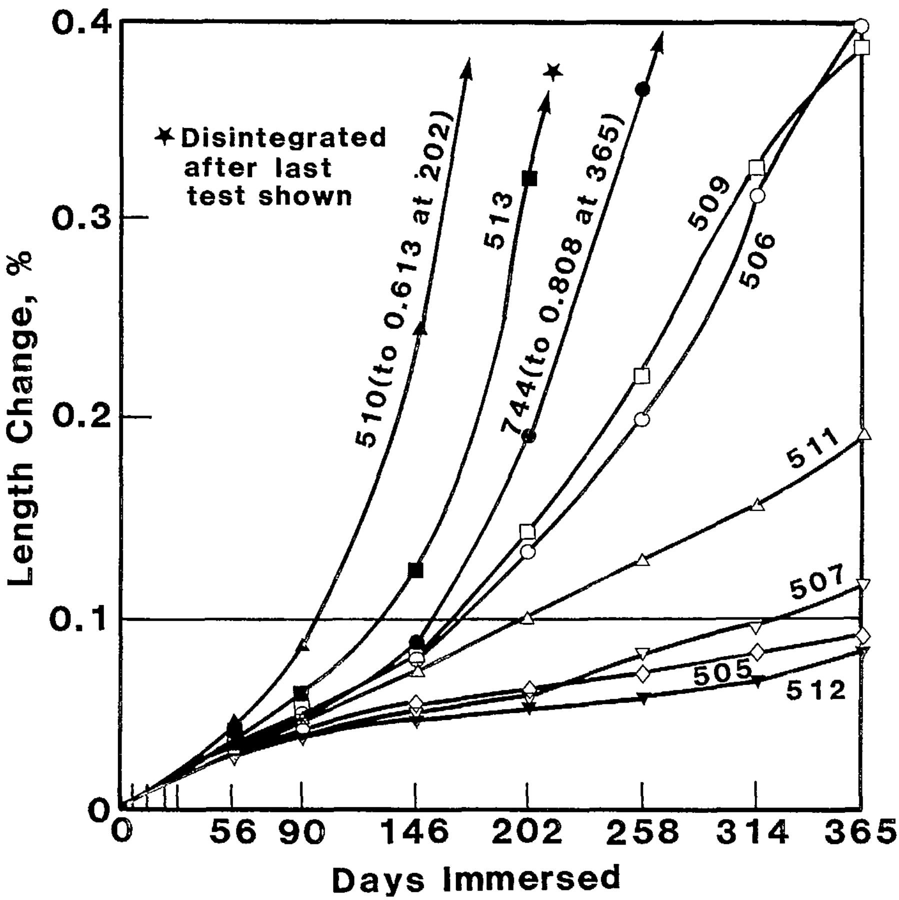

Fig. 7.25 — Effects of fly ash on expansion of mortar prisms incorporating non-sulphate-resisting cement in sulphate solution (183)

Key: 744 = Cement with calculated C_3A, 9.4%

Remaining numerals indicate replacement of cement 744 by 30% of eight different, but unidentified, fly ashes (183).

Mather summarized the findings of the study-in-progress as follows:

> "... what seems to be suggested (by the results) is that a pozzolan of high fineness, high silica content and highly amorphous silica is the most effective pozzolan for reducing expansion due to sulphate attack on mortars made with non-sulphate resisting cements... The pozzolans that resulted in poorer performance ... were in 6 of 7 cases fly ashes produced by the combustion of lignite."

It might be added that the ranking of subbituminous ashes as better than the one bituminous ash examined is in direct contradiction with the findings of Dunstan (179,180). However, in the absence of detailed properties of the ashes examined and without comparable data from mortars made with other fly ashes, it would not be advisable to draw further conclusions from this report. Clearly, the influence of fly ash on the sulphate resistance of concrete is not completely understood, and much more research should be conducted to establish guidelines on this important aspect of concrete durability.

Effects of Fly Ash on Alkali-Aggregate Reactions in Concrete

Shortly after he discovered that alkali-aggregate reactivity was a cause of expansion and damage in some concretes, Stanton (184) reported that the effects could be reduced by adding finely ground reactive materials to the concrete mix. Subsequently, a variety of natural and artificial pozzolans and mineral admixtures, including fly ash, have been found to be effective in reducing the damage caused by alkali-aggregate reactions (AAR). As discussed below, the effectiveness of fly ash (and other mineral admixtures) in controlling AAR appears to be limited to reactions involving siliceous aggregates. A second form of alkali-aggregate reaction, alkali-carbonate reaction, has been reported (185) and has been shown to be relatively unresponsive to control by the addition of pozzolans (186).

It is not within the scope of this review to consider the many and complex aspects of AAR; these matters are the subject of much current research and are poorly understood. Rather, consideration has been limited in this review to some aspects of the subject directly relevant to the selection of fly ash as a means to control alkali-silica reactivity.

The effectiveness of fly ash in the control of alkali-silica reactivity has been widely reported. Pepper and Mather (187) reported the minimum percentage replacement (by volume) of cement by fly ash required to reduce expansion in test specimens by 75%. Their results are shown in Table 7.9.

Table 7.9 — Mimimum percentage replacement of fly ash*

Replacement material	Minimum percentage (by volume) replacement for effectiveness		
	14 days	6 months	average
Fly ash I	46	36	41
Fly ash II	48	36	42
Fly ash III	52	36	44
Fly ash IV	45	34	40

*From reference 187.

Elfert (62) reported data of a similar nature from work carried out at the U.S. Bureau of Reclamation (Figure 7.26).

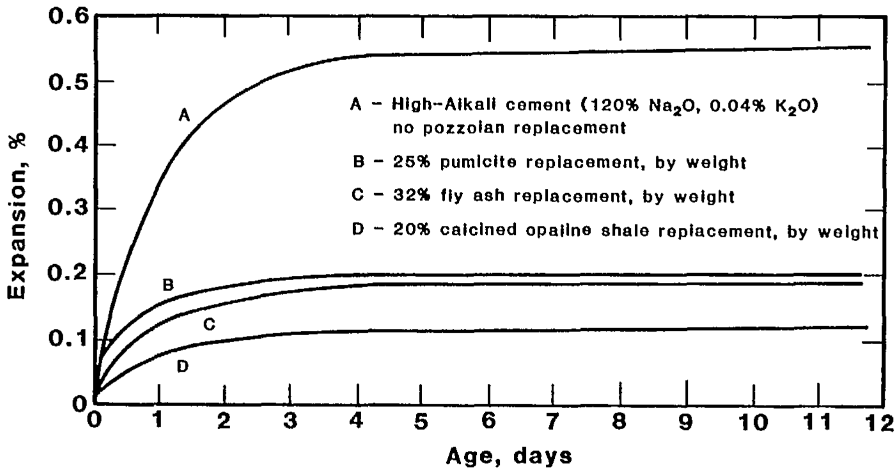

Fig. 7.26 — Effect of pozzolan on reactive expansion of mortar made with alkali cement and crushed Pyrex glass (62)

While it is clear that some fly ashes are effective in controlling alkali-aggregate expansion, it is questionable whether the early strength losses caused by replacement of 40 to 50% of the cement by low-calcium fly ash would be tolerable for more than a limited number of applications. Similar levels of replacement using high-calcium fly ashes may be more acceptable.

During a study of alkali-reactive aggregates in Nova Scotia, Duncan et al. (188) showed effective suppression of expansion by replacement of moderate alkali cement — 0.71% as Na_2O — with as little as 25% of fly ash. Some data are shown in Figure 7.27.

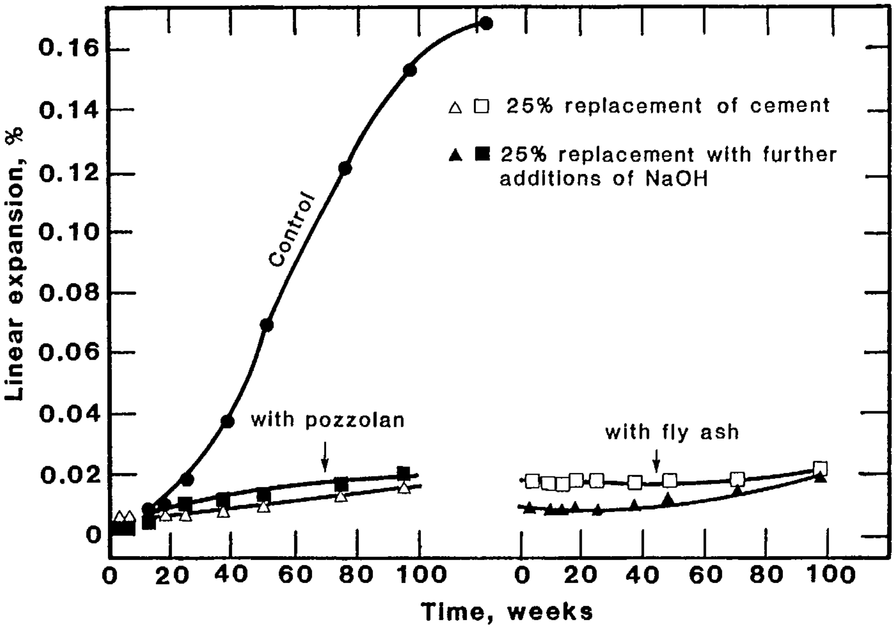

Fig. 7.27 — Expansion of concrete prisms made with metagreywacke aggregate and 25% cement replaced with pozzolan (188)

In more recent studies, the following factors have been identified as particularly important:

— the concentration of soluble alkali in the system;

— the type of aggregate;

— the quantity of fly ash used.

It is now generally accepted that, with regard to alkali-silica reactivity, it is the concentration of soluble alkali, rather than the total alkali content of the system that affects expansion. Figure 7.28 shows the relationship between water soluble alkali content and the time required for cracking in concrete containing Beltane opal as aggregate, as reported by Hobbs (189).

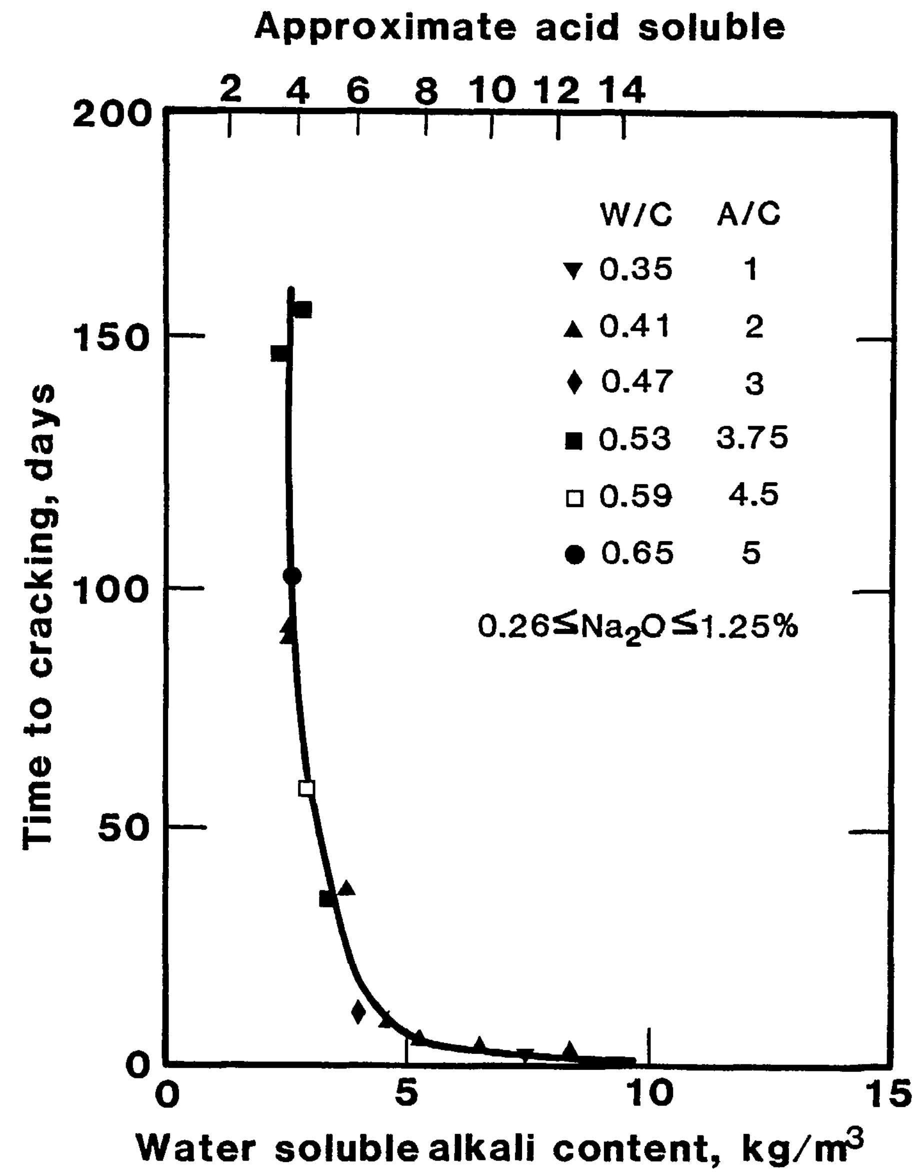

Fig. 7.28 — Variation in time to cracking with water soluble alkali content at the most critical alkali-beltane opal ratio (189)

In general, Hobbs estimated that the lower limit of alkali concentration at which mortar test specimens exhibit excessive cracking was 3.4 kg/m^3 as acid-soluble alkali (190). This is equivalent to 2.5 kg/m^3 as water-soluble alkali (189).

The source of alkali (as Na_2O or K_2O) is not regarded as important. Thus soluble alkali from fly ash is regarded as equally deleterious as that from portland cement. This is particularly important with regard to the use of high-calcium fly ashes containing large amounts of soluble alkali sulphates. These have been reported (93) to increase rather than decrease the rate of deterioration through alkali-silica reactivity.

Not all aggregates are susceptible to alkali-silica reactivity nor do all susceptible aggregates behave in the same way. Alkali-silica reactivity is a long-term process that has been found to occur most commonly with aggregates that contain non-crystalline or crypto-crystalline silica.

Aggregates and their mineralogical constituents known to react with alkalis in concrete include (191):

— the silica materials: opal, chalcedony, tridymite, cristobalite;

— zeolite;

— heulandite;

— glassy to crypto-crystalline rhyolites, dacites, andesites and their tuffs;

— certain phyllites.

In Britain, the main reactive component of aggregates susceptible to alkali-silica reactivity has been found to be chert (flint) (192). In South Africa, studies have been made on hornfels of the Malmesbury Group (193).

Much of the experimental work in the literature has been directed to the study of very reactive, porous, opaline aggregates, such as the Beltane opal from California, or to Pyrex glass. Both are generally more reactive than many of the natural aggregates encountered in practice, and this should be considered when the reported data are being evaluated from the perspective of practical applications.

As with most other aspects of fly ash utilization, ashes from different sources behave significantly differently in their effects on alkali-silica reactivity. As was noted above, some high-calcium fly ashes have been found in the laboratory to be ineffective or deleterious in relation to alkali reactivity.

In studies using Beltane opal, Hobbs (194) reported the data shown in Figure 7.29 for fly ashes with the chemical compositions summarized in Table 7.10. The following conclusions were drawn by the author from these experiments:

— "The partial replacement of a high-alkali cement by fly ash reduced the long-term expansion due to alkali-silica reactivity but, even when 30 or 40% of the cement was replaced, most of the blended cement mortars cracked at earlier or similar ages to the portland cement mortars.

— "The effectiveness of the fly ashes in reducing long term expansion varied widely. It is suggested that the effectiveness of the (fly ashes) may be dependent upon their alkali content or fineness.

— "Where part of the cement was replaced by fly ash, the lowest mortar alkali content, expressed as equivalent Na_2O, at which cracking was observed was 2.85 kg/m^3. This figure relates only to the acid soluble alkalis contributed by the portland cement and compares with a figure of 3.5 kg/m^3 for a portland cement mortar.

— "If it is assumed that fly ash acts effectively like a cement with an alkali content of 0.2% by weight, the lowest alkali content at which cracking was observed was 3.4 kg/m^3.

— "Both fly ashes and granulated blast furnace slags act as alkali diluters, slags being more effective in reducing damage due to alkali-silica reactivity than fly ash.

— "From the above it may be concluded that, when the aggregate to be used contains a reactive constituent and when the concrete is to be exposed to external moisture, damage due to alkali-silica reactivity is unlikely to occur if the acid-soluble equivalent Na_2O content of the concrete is below 3 kg/m^3. In calculating the alkali content of the concrete, granulated blast furnace slags may be assumed to contain no available alkalis but fly ash should be assumed to have an available alkali content of 0.2% by weight."

Table 7.10 — Composition and properties of fly ashes examined by Hobbs*

	Fly ash number			
Composition, %	1	2	3	7
SiO_2	50.02	51.48	46.58	49.72
Fe_2O_3	9.02	8.70	14.24	5.22
Al_2O_3	26.83	28.08	25.22	32.45
CaO	1.48	1.27	4.10	2.77
MgO	0.93	0.93	0.95	2.41
SO_3	0.79	1.15	1.29	0.53
LOI	3.43	1.74	1.84	3.24
Na_2O (total)	0.88	1.13	0.80	0.38
Na_2O (water sol.)	0.07	0.10	0.08	0.02
K_2O (total)	3.90	3.85	2.35	1.40
K_2O (water sol.)	0.07	0.11	0.04	0.02

*From reference 194.

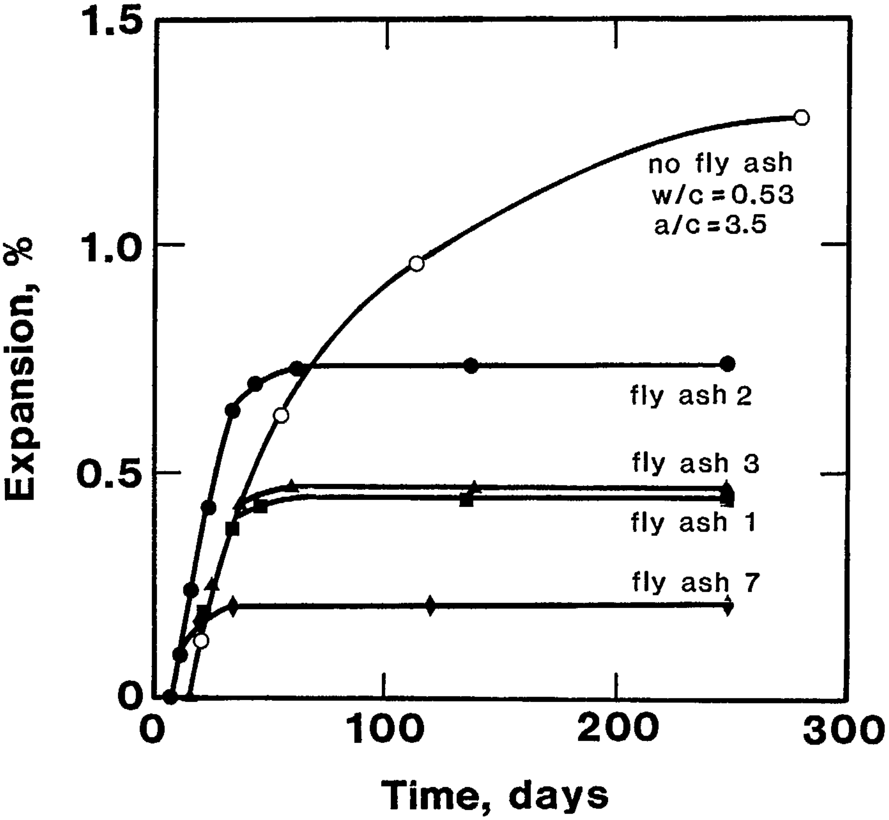

Fig. 7.29 — Variation in expansion with age for specimens where part of the aggregate was replaced with fly ash (194)

In experiments using Pyrex glass, Nixon and Gaze (192) presented the data shown in Figure 7.30 and drew the following conclusions:

— "When Pyrex glass is used as the reactive aggregate the partial replacement of a high alkali portland cement by fly ash or by granulated blast furnace slag produces a significant reduction in expansion of mortar bars at all replacement levels tested (10, 20 and 30 per cent fly ash). The reductions are greater than could be accounted for by simple dilution of the alkali content of the portland cement.

— "Weight for weight the fly ashes are more effective (than granulated slag) in reducing expansion ...

— "Only small differences were found between the effectiveness of different fly ashes. These differences could best be correlated with a measure of the pozzolanicity of the ash. The ashes with lower alkali content did, on the whole, seem to perform slightly better than those with high alkali (content) but this effect was secondary to the pozzolanicity. The available alkali content of the ashes gave no better correlation with the observed expansions than did the total alkali content ...."

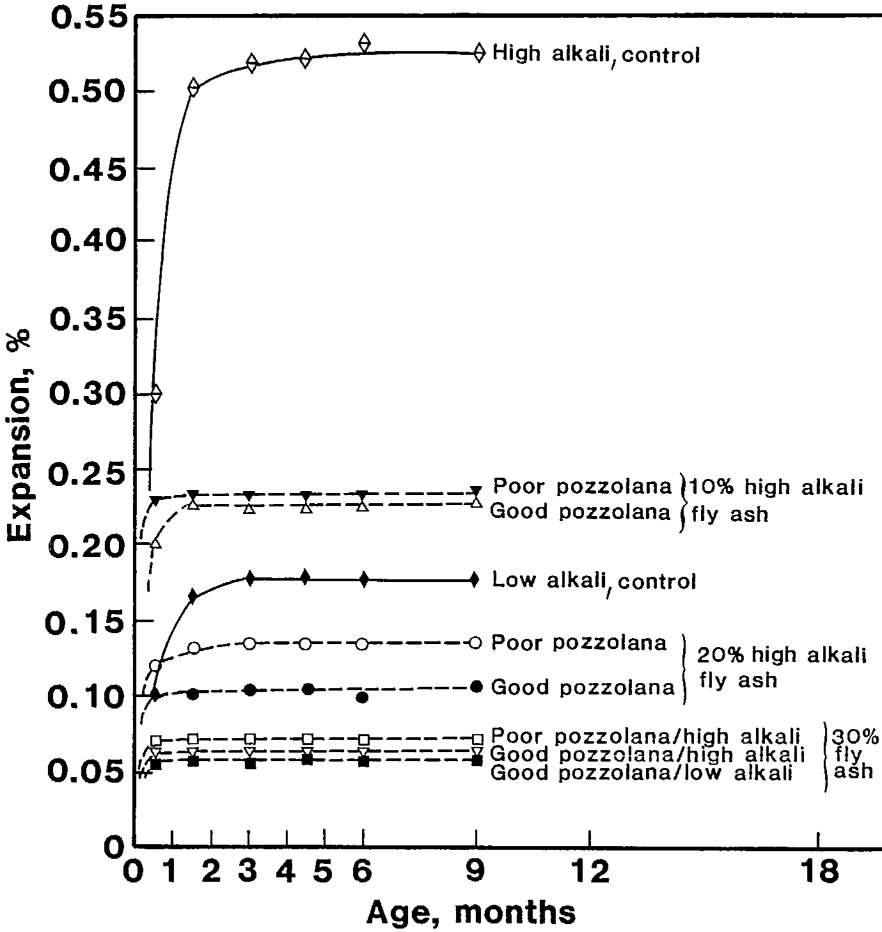

Fig. 7.30 — Expansion of mortar bars containing high-alkali cement and fly ash with Pyrex aggregate (192)

The same authors (195) reported on studies using chert aggregate in fly ash concrete prism specimens and presented the data shown in Figure 7.31.

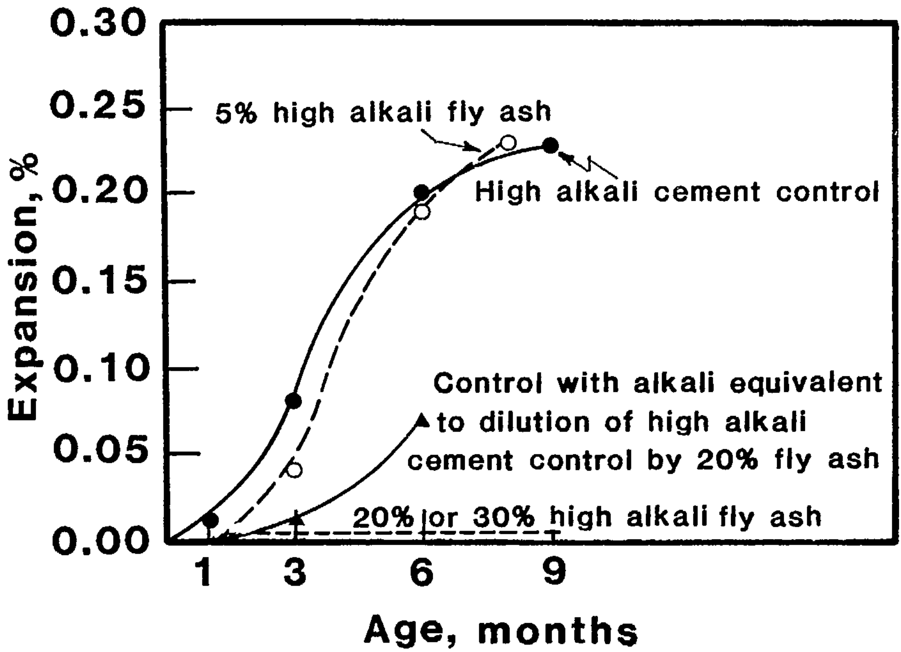

Fig. 7.31 — Expansion of concrete prisms containing high-alkali cement and fly ash with 30% flint/quartz aggregate (195)

Oberholster and Westra (193) studied alkali-silica reactivity in the Malmesbury Group aggregates and examined, among many additives, a low-calcium fly ash. The authors reported the fly ash to be more effective in reducing expansion than would be expected for a simple dilution of alkali content.

The study by Oberholster and Westra (193) included an examination of concrete prisms, for which it was found that the fly ash effectively suppressed expansion at cement replacement levels of 20% or more on an equal volume basis.

Stanton (184), Porter (196), and Pepper and Mather (187), in early studies of the use of fly ash to reduce expansion caused by alkali-silica reactions, noted that small additions of fly ash to mortars containing an opal aggregate may increase expansion, whereas larger amounts may result in reduced expansion. The general form of the relationship between ash quantity and expansion observed by these workers is illustrated in Figure 7.32.

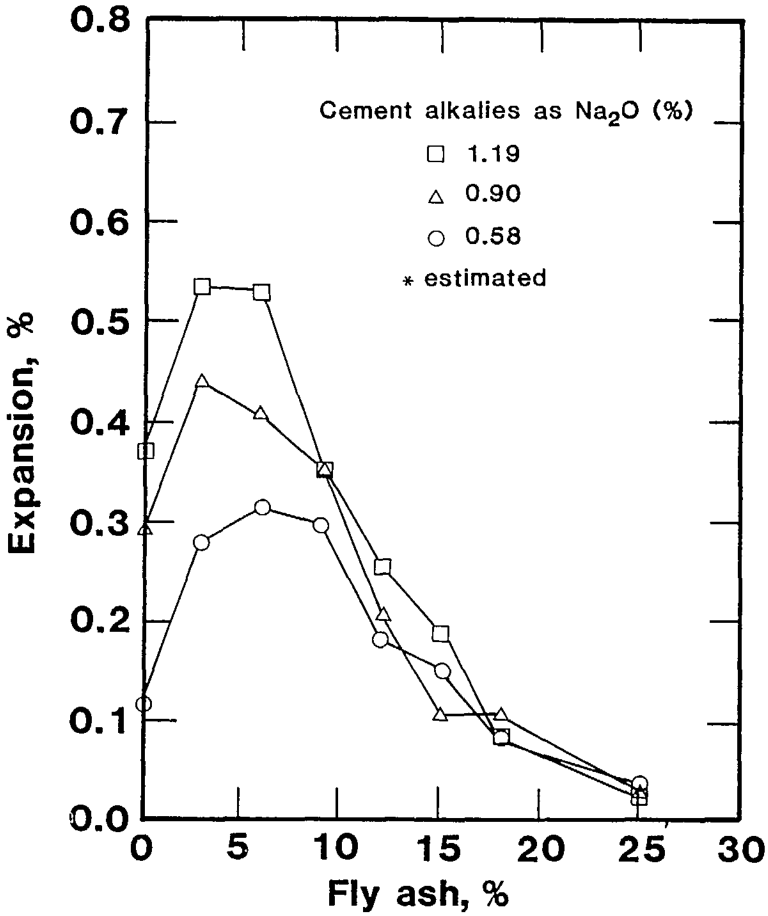

Fig. 7.32 — Effect of cement alkalis and fly ash on alkali-aggregate reaction (191)

In a more recent study, Hobbs (197) reported that replacing 5% by weight of portland cement by four fly ashes, a ground slag or limestone fines had little effect upon the expansion of mortar bars tested at a critical alkali-silica ratio.

Dunstan (191) has examined 17 fly ashes of both bituminous and sub-bituminous origin using Pyrex glass as aggregate. Among other conclusions, Dunstan suggested that the expansion/fly ash replacement relationship takes the form shown in Figure 7.33 and that the amount of fly ash corresponding to the pessimum point (the point of maximum expansion) was related to the CaO content. As CaO increased so the pessimum point increased with respect to fly ash replacement. This would lead to the conclusion that high-calcium fly ashes would show increased contribution to expansion at the levels of replacement normally used with low-calcium fly ashes and would only become effective in retarding expansion caused by alkali-silica reactions at higher replacement levels.

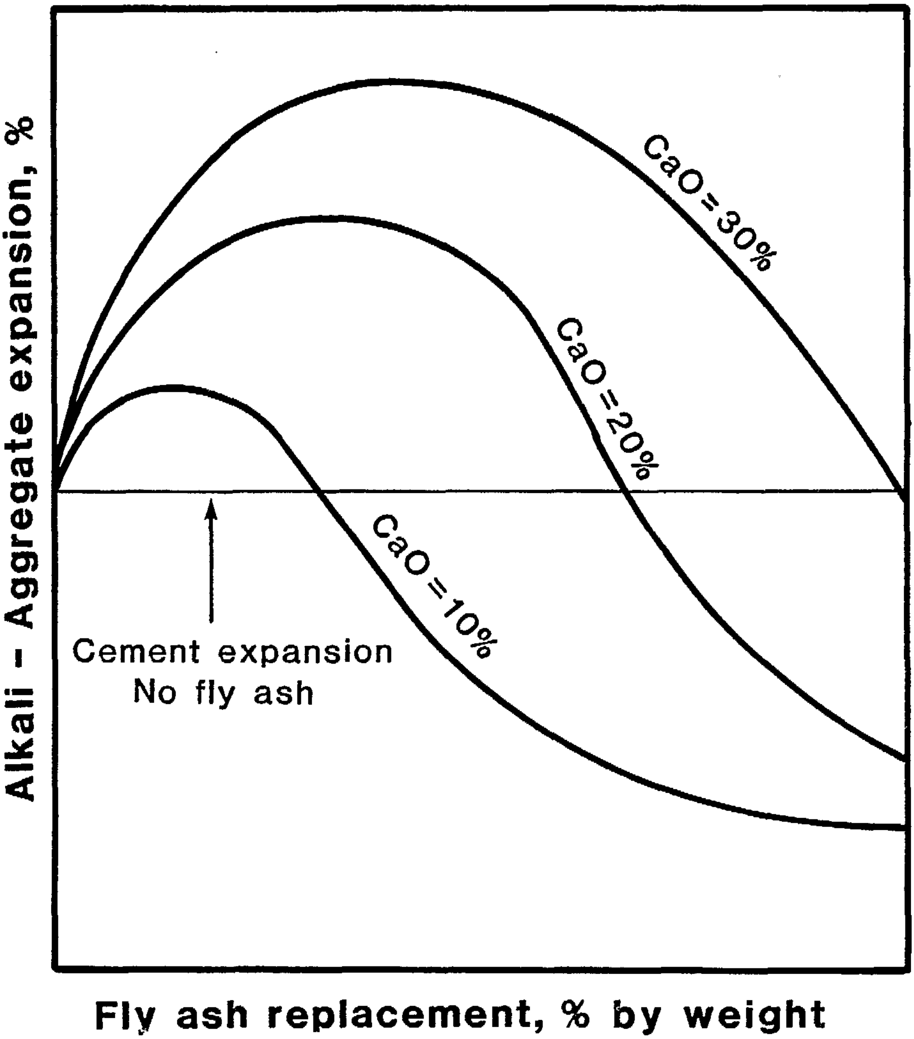

Fig. 7.33 — Theoretical expansion due to alkali-aggregate reaction (191)

In summary, the following points may be made:

— There are substantial published data to show that low-calcium fly ashes are effective in reducing expansion caused by alkali-silica reactions when used at a replacement level in the range from 25 to 30%.

- — The use of high-calcium ashes has received less attention and, hence, the background information relevant to their employment is less well developed. If they are to be used, there is some indication that effective replacement levels may be higher than for low-calcium ashes. Depending upon their ability to develop strength at early ages, concretes made with high fly ash replacement levels may or may not be acceptable.
- — The mechanism and details of control of expansion caused by alkali-silica reactions are not fully understood, and there remains much research to be carried out before a satisfactory understanding can be developed.

Effects of Fly Ash on Corrosion of Reinforcing Steel in Concrete

Recently the corrosion of steel-reinforcing members has become an issue of concern with regard to the use of fly ash concrete in structures subject to corrosion caused by exposure to chloride ions from de-icing salts or sea water.

If the concrete cover over steel reinforcement is sufficiently thick and impermeable, it will normally provide adequate protection against corrosion. The protective effect is of both a physical and chemical nature in that the concrete functions in three ways:

- — It provides an alkaline medium in the immediate vicinity of the steel surface.
- — It offers a physical and chemical barrier to the ingress of moisture, oxygen, carbon dioxide, chlorides, and other aggressive agents.
- — It provides a relatively electrically resistive medium around the steel members.

Under alkaline conditions (pH in excess of approximately 11.5), a protective oxide film will form at a steel surface that renders it *passive* against further corrosion.

When concrete carbonates (see above), if the depth of neutralization reaches the steel/concrete boundary, passivation may be reduced and corrosion may occur if sufficient oxygen and moisture can reach the metal surface. Chlorides or other ions may also destroy the protective action of passivation and encourage corrosion.

The Rilem Technical Committee on Corrosion of Steel in Concrete (198) made the following statements that serve to give perspective to this issue:

— "The efficacy of the (concrete) cover in preventing corrosion is dependent on many factors which collectively are referred to as its 'quality.' In this context, the 'quality' implies impermeability and a high reserve of alkalinity which satisfies both the physical needs and chemical requirements of the concrete cover. If the concrete is permeable to atmospheric gases or lean in cement, corrosion of the reinforcement can be anticipated and good protection is attempted by the use of dense aggregate and a well compacted mix with a reasonably low water-cement ratio.

— "If chloride corrosion is excepted, it is now usually agreed that carbonation of concrete cover is the essential condition for corrosion of reinforcement."

As was discussed in a previous section of this chapter, the issue of carbonation of fly ash concrete has received some attention in recent years. However, it is the authors' opinion that carbonation of fly ash concrete is not a matter of concern if attention is given to obtaining adequate impermeability in the concrete mass.

In 1950, the question was raised (199) as to whether there was a possibility of corrosion of reinforcing steel in fly ash concrete by the sulphur-containing components of fly ash. Gilliland (200) noted that most of the sulphur in fly ash is present as sulphate and, therefore, would have an effect similar to the sulphate components in portland cement. Further, he pointed out that corrosion of steel is greatly affected by pH — at the high pH prevailing in concrete, corrosion rates would be expected to be slow. Ryan (201) presented further information on the same point and drew the following conclusions:

— "Sulphur compounds in fly ash are usually so limited by specifications that they are not materially different in the concrete, whether fly ash is used or not. Moreover, the alkaline condition in the concrete is unfavourable to a sulphate attack on steel.

— "Carbon in fly ash would appear by theoretical considerations to be much more significant in concrete than is sulphur. The actual effect should be investigated. However, if it is kept under 3 per cent in the fly ash, its percentage in the concrete becomes so small that if it is well dispersed its effect on the electrical conductivity of the concrete, and therefore upon the corrosion of the steel, should be quite minor."

These conclusions seem to be generally acceptable in the light of reported research which has shown that fly ash concrete does not decrease the corrosion protection of steel reinforcing when compared with normal concrete (50,202,203). One recent study by Larson et al. (204,205) has found that corrosion protection is increased by the inclusion of fly ash in concrete.

In regard to the quality of concrete cover to steel and the points raised by the Rilem Technical Committee (see above), fly ash may influence both permeability and the alkalinity of the system.

The permeability of fly ash concrete and the related issue of carbonation have been discussed in previous sections of this report. It is sufficient here to reiterate that properly proportioned fly ash concrete, subjected to adequate curing, should in general be less permeable at late ages than corresponding plain concrete. The danger of permeability lies in the exposure of fly ash concrete to aggressive agents before it is mature, either as a result of inadequate proportioning, incomplete curing, or poor fly ash quality.

With regard to alkalinity, it has been suggested that because the pozzolanic reaction consumes calcium hydroxide, as it progresses, this may cause a decrease in the pH of the pore water in fly ash cement paste. The pore solutions in hydrated cement are highly alkaline and, as Diamond (206) has shown, this results from the presence of sodium and potassium ions rather than from the presence of calcium hydroxide. In studies of two fly ash cement systems, Diamond showed (206) that the alkalinity is determined almost totally by dissolution of sodium and potassium salts from cement; at quite early ages, the concentration of calcium in solution is reduced to very small levels. In the samples studied by Diamond, pore solution pH was reduced from 13.75 in a control system to about 13.55 in the presence of fly ash.

Effects of Fly Ash on Concrete Exposed to Sea Water

The deterioration of concrete in marine environments is a complex subject and cannot be treated adequately in a review such as this. This discussion has been limited to an examination of some of the aspects of using fly ash in marine concrete, with regard to the rather limited amount of directly applicable published data, and some extrapolations from the many reports that have been published on the behaviour of plain concrete in the sea.

Exposure of concrete to the marine environment subjects it to an array of severely aggressive factors, including most of those discussed in the preceding sections of this chapter.

Concrete in the tidal zone, subjected as it is to alternating wetting and drying; wave action; abrasion by sand and debris; frequent cycles of freezing and thawing; corrosion of reinforcement; all occurring in a chemically aggressive medium, is the most severely attacked. Permanently immersed concrete is less severely affected (207,208).

Very little direct observation of fly ash concrete in sea water has been reported in the literature, although research in this regard is in progress (209). Because of the present lack of information, it is perhaps permissible to speculate, on the basis of the previously considered effects of fly ash on concrete durability and in an effort to obtain some guidance, as to the likely consequence of using fly ash in marine concrete.

Concrete in the sea is subjected to the aggressive influences discussed above. In Table 7.11 these have been compiled to give a profile of the ways in which fly ash concrete might be affected by exposure to sea water.

Table 7.11 — Potential influence on fly ash concretes of aggressive agents contained in sea water

Form of attack	Influence of fly ash	Notes
Wetting/drying	None	If proportioning and curing adequate.
Freezing/thawing	None	If proportioning, air-entrainment and curing adequate.
Sulphate	Improved by low-calcium ash.	
Alkali-aggregate	Acts to reduce expansion.	
Corrosion of steel	None	If porportioning and curing adequate.
Permeability	Improved at late ages.	If proportioning and curing adequate.
Magnesium salts	Not known.	

Whereas it is considered that permeability is the major factor affecting the durability of concrete in sea water (208), it is evident from the above that fly ash has the potential to contribute to a number of aspects of concrete durability in the marine environment. It is clear also that this is an aspect of fly ash concrete behaviour that is greatly in need of research.

8. STANDARDS AND SPECIFICATIONS FOR THE USE OF FLY ASH IN CONCRETE

"Since it is the mineralogical composition, and not the chemical composition, which would govern the pozzolanic and cementitious behaviour of a mineral admixture, classifications and specifications emphasizing the chemical composition are more of a hindrance than a help in promoting the use of mineral admixtures in cement and concrete industries. New classifications, specifications and accelerated tests ... that are capable of relating the desired performance criteria to the microstructure of the hydrated cement paste containing the admixture are urgently needed." — P. Kumar Mehta (93).

A number of countries have published national standards and specifications regulating the use of fly ash in concrete. In some cases, these have been adapted from standards developed to control the use of natural or calcined pozzolans, while in others, new standards specifically directed to fly ash or other supplementary cementing materials have been established. Recent comparative reviews of national standards have been published by Manz (210) and Rossouw and Kruger (211). Table 8.1 presents a compilation of the designations of the relevant national standards and specifications from 9 countries. A summary of the main technical features of these standards is given in Tables 8.2 to 8.4.

The development of standards is an ongoing process that largely comprises the establishment of a consensus among different interests. It is a difficult task because materials such as fly ash frequently come into use long before their properties and qualities are fully understood. In addition, because there is little international trade in fly ash, there has been no need for consistency to be established between the national standards of different countries. Unfortunately, this has also resulted in a lack of consistency in terminology (212-219).

Table 8.1 — Designations of national standard specifications for fly ash for use in concrete*

Country	Designation of Standard	Year	Reference**
Australia	A.S. 1129	1971	(212)
Austria	Onorm B3320		(213)
Canada	CAN3-A23.5-M82	1982	(5)
India	I.S. 1344-1968	1968	(214)
Japan	JIS A 6201	1967	(215)
Korea	K.S. L5405		(216)
U.K.	B.S. 3892, Parts 1 & 2 Revisions	1963 1982	(217)
USA	ASTM C 618-83	1983	(6)
USSR	GOST. 6269-63	1963	(218)

*From references 210, 211.
**Citations are to the most recently published revisions known to the authors.

Table 8.2 — Chemical requirements for fly ash for use in concrete*

			Canada Class		Britain						USA Class		
	Australia	Austria	F	C	B.S. 3892	Draft	India	Japan	Korea	Turkey	F	C	USSR
Free water (% max)	1.5	1.0	3.0	3.0	1.5	0.5		1.0	3.0	3.0	3.0	3.0	
LOI (% max)	8.0	5.0	12.0	6.0	7.0	7.0	12.0	5.0	12.0	10.0	12.0	6.0	10.0
MgO (% max)		5.0			4.0	4.0			5.0	5.0	5.0	5.0	
Sulphate (as % SO_3 max)	2.5		5.0	5.0	2.5	2.5	3.0		5.0	5.0	5.0	5.0	3.0
Total sulphur (as % SO_3 max)		3.5											
SiO_2 (% max)		42-60						45				40	
Al_2O_3 (% max)		16-32											
Fe_2O_3 (% max)		3-12											
Minimum S+A+F**							70		70	70	70	50	
CaO (% max)		5-20								6.0			
Free CaO (% max)		2.0											
Total Alkalies (as % Na_2O max)									1.5				
Available Alkalies (as % Na_2O max)							1.5				1.5	1.5	
Carbon (% max)		3.0											
Chloride (% max)		0.1											

*From references 210, 211.
**Sum of % SiO_2 + % Al_2O_3 + % Fe_2O_3.

Table 8.3 — Physical requirements for fly ash for use in concrete*

			Canada Class		Britain						USA Class	
	Australia	Austria	F	C	BS 3892	Draft	India	Japan	Korea	Turkey	F	C
Specific surface (Blaine, min. cm^2/g)		4-5000					2800	2400				
Sieve (max %; μm)**	10;150		34;45			12.4;45				0.3;200 8;87		34;45
Av. particle diam. (μm)									9			
Specific Gravity (min)								1.95				

*From references 210, 211.
**Sieve requirements are expressed as the maximum permitted quantity of material (as a percentage) retained on a screen of specified aperture (expressed in μm units); e.g., a maximum permitted quantity of 34% retained at 45 μm is expressed as 34;45.

Table 8.4 — Performance requirements for fly ash for use in concrete*

		Canada Class		Britain						USA Class	
	Austria	F	C	B.S. 3892	Draft	India	Japan	Korea	Turkey	F	C
POZZOLANIC INDEX:											
With cement (min % of control, 28 day)	80	75					60/70	85	70	75	75
With cement (min % of control, 7 day)		68									
Lime (min MPa)						3.9		5.5		5.5	5.5
Sand Replacement									100		
Water requirement (max % of control)					95			102	105	105	105
SOUNDNESS:											
Autoclave expansion (max %)		0.8				0.8		0.5		0.8	0.8
Other tests	pat								10**		
Drying shrinkage (max % at 28 days)						0.1					
Drying shrinkage (increase over control %)		.03						.03		.03	.03
Alkali reactivity (max % expansion at 14 d)								.02		.02	.02
Alkali reactivity (max % redn. of expansion)		60									

*From references 210, 211.
**Le Chatelier expansion test.

Terminology and Classification of Fly Ashes

In general, the term *fly ash* appears to be accepted in English-speaking countries other than Britain where *pulverized fuel ash* (abbreviated to PFA) is employed. In French, *cendres volantes*, in German, *flugashe*, and in Spanish, *cenizas volantes*, are commonly used terms.

Until recently, fly ash was regarded as a pozzolan. However, as high-calcium fly ashes have become more widely used, it has been realized that not all of them require an external source of lime in order to produce cementitious properties, and, hence, are not strictly pozzolans. Manz (210) and others have suggested that the high-calcium fly ashes (the so-called Class C ashes) are best distinguished from the low-calcium (Class F) ashes by their cementing properties. Thus, a general term *mineral admixtures* has been suggested to describe all classes of slags, ashes, pozzolans, and other cement supplements, with a further distinction being drawn on the basis of their self-cementing capabilities. This form of classification has been proposed as being preferable to the current division of fly ashes into two classes, according to the rank of coal from which they originate, that is practised currently in Canadian (5) and U.S. (6) standards.

Use of the term *mineral admixtures* has been criticized in the past as reflecting that use of these materials might be relegated to small quantities of *addition*, as is normally the case for chemical admixtures.

In Canada, the term *supplementary cementing materials* has been adopted in specifications (5). While being somewhat long, it has the virtue of describing precisely the role of these materials in most concretes.

Nature of Specifications for Fly Ash in Concrete

In general, there are two issues to be considered when examining specifications for materials such as fly ash:

- — the degree to which the selection of properties regulated by the specification serves to protect the user from incorrect or inappropriate use of the product;
- — the degree to which the test methods proposed for examination of these properties are suitable to the evaluation of the materials and are adequate to detect and exclude unsuitable materials.

On examining the national standards from many sources, it is clear that there is general (though not always well-substantiated) agreement that the following properties should be considered when assessing the suitability of fly ash for use in concrete:

— pozzolanic activity

— particle size or surface area

— carbon content or loss on ignition

— moisture content

— various chemical parameters.

For simplicity in specification documents, these qualities are frequently divided between chemical and physical requirements. Because some of the so-called physical requirements relate to the chemical activity of fly ash, a more appropriate distinction might be drawn between chemical requirements, physical properties, and performance requirements, and this approach has been adopted in this chapter.

Chemical requirements

Many national standards reflect the concern that components harmful to the properties or durability of concrete should not be introduced with fly ash. Some go further, and attempt to relate the performance of fly ash as a pozzolan to chemical composition. The following chemical requirements are frequently specified.

Moisture content: With the exception of India and the U.S.S.R., standards from most countries place limits on moisture content. This reflects largely a need to protect the purchaser from receiving ash in a wet state.

Loss on ignition is specified in all national standards, with the intention of limiting carbon content, the presence of which has been associated with difficulties in control of air-entrainment in fresh concrete (see Chapter 3). Loss on ignition is not a reliable parameter for this purpose because a number of other components in fly ash are volatile or decompose on heating.

Direct methods of determining carbon content are available using rapid tests and provide a more reliable measure of the presence of carbon in ash.

The distinction between loss on ignition (set at 5% max) and carbon (set at 3% max) is drawn explicitly in the Austrian national standard.

Sulphate: Most national standards limit the concentration of sulphate introduced into concrete with fly ash. This is done to prevent interference with the setting of cement and to reduce the possibility of expansive deterioration of the hardened concrete. Similar limitations are usually placed on other concrete components. There is no general agreement between national standards as to the level of sulphate permissible in fly ash.

Magnesium oxide: Although there is no evidence that magnesium in fly ash is present in the form of periclase (MgO), many standards reflect the same limitation on MgO content that is applied to portland cements.

Available alkalis: The concentration of alkalis in cementitious materials is frequently limited to prevent efflorescence and to control alkali-aggregate reactions. Excessive sodium or potassium content in fly ash may contribute to efflorescence in hardened concrete. Winer and Malhotra (220) have examined accelerated test methods for the determination of soluble alkalis, that are more readily applicable to high-calcium fly ashes than the presently specified tests.

Chloride: Only the Austrian specification for fly ash limits chloride (to a maximum of 0.1%) in fly ash. In view of the role of chloride in the corrosion of steel reinforcement, some investigation of the need to consider chlorides in fly ash may be required in North America.

Major oxides: Some standards require that the silica content of fly ash be in excess of a specified minimum value, while others require the sum of the alumina, silica, and iron oxide content to be in excess of a minimum value. It has been suggested (221) that the sum ($SiO_2 + Al_2O_3 + Fe_2O_3$) is related to the quantity of glassy particles in fly ash. There is no evidence that the content of these oxides is directly related to the performance of ash in concrete (91,93).

Physical properties

Except in the U.S.S.R., national standards for fly ash require control of fineness either through particle size or surface area. Although not generally specified, some form of mass–volume relationship is usually required as a part of the tests used to determine pozzolanic activity and may be required to establish uniformity of an ash source.

Particle size or surface area: There is general agreement that pozzolanic activity is affected by the particle size distribution or fineness of fly ash, and there is considerable evidence that the presence of coarse particles in ash is deleterious (see Chapters 3 and 4). There is, however, disagreement about the method of testing and the limits to be placed on coarse particulate content from one standard to another.

In general terms, the particle size properties of a material such as fly ash may be measured by one of three types of test:

— wet sieving

— dry sieving

— air permeability.

Australian, Canadian, British, U.S., and Turkish standards require the use of wet-sieving methods to determine the residue on one or more screens of specified mesh size.

The Turkish and the Australian standards both require the use of two screens. Other standards are restricted to determination of retention on a 45-μm screen.

The wet screen techniques, while convenient in that they employ inexpensive equipment, may produce erroneous data with ashes containing substantial water soluble materials or components that react with water. The use of wet methods with high-calcium fly ashes should be considered in this regard.

A simple, but more expensive, technique that is not subject to the influences of water is the dry sieve method using the Alpine Air-Jet Sieve. Details of the method and its comparison with conventional methods for determination of fineness of cement were reported by Malhotra and Zoldners (222). A direct comparison of wet and dry screening of ten different fly ashes was made by Berry and Hemmings (223). It was found that correlation between fineness as determined by the Alpine Air-Jet Sieve and the wet screen (ASTM C430) was excellent, but that the wet screen consistently gave a value for the quantity retained at 45 μm in excess of that found for the dry method. In Canada, the Alpine Air-Jet method is currently used on a routine basis by Ontario Hydro for quality control of ash fineness.

A much less satisfactory approach to fineness control, still commonly used, is to specify *surface area* as determined by air permeability. This is less valuable for a number of reasons:

- Surface area is not a definable physical property for fine particles unless it is related to the method of measurement.
- Methods of determination based on air permeability, such as are used for portland cements, are not reproducible with most fly ashes.
- There is no clear relationship between surface area as determined by the more common methods and strength development in fly ash concretes.

Mass/Volume Relationships: For practical reasons, it is necessary to know the approximate volume occupied by a given mass of fly ash. Because most fly ashes contain hollow particles, none of the displacement methods used measures true particle density. The property determined is usually one form or another of apparent density.

Performance Requirements

Ideally, specifications for materials such as fly ash should be based upon measurements of performance. Unfortunately, those performance qualities that are most frequently required are among the most unreliable aspects of the specifications regulating fly ash use.

The most frequently specified requirements reflect attempts to determine the pozzolanic activity of fly ash and its effect on water demand, its potential for alkali-reactivity, and its influence on soundness and shrinkage. Of these, alkali-reactivity, soundness, and shrinkage determinations generally follow the approaches taken in corresponding specifications regulating the properties of cements.

Pozzolanic activity is the most difficult of the fly ash properties to define and to determine, largely because it is not understood. Pozzolanic activity comprises the reaction of an alumino-silicate with calcium hydroxide to form cementitious products; it is usually determined by one or more of the following classes of test:

- — determination of the relative strength of fly ash and control mortars after curing for 28 days;
- — determination of the relative strength of fly ash and control mortars after curing for 7 days under accelerated conditions;
- — determination of the strength of fly ash–lime mortars after curing for 27 days.

In general, it is agreed that these tests are an inadequate means to predict fly ash performance in concrete. Their inadequacy results principally from the fact that the strength of a cemented composite is not determined solely by the extent of the formation of cementitious components. Other factors are involved and generally cannot be accounted for in the normal test procedure.

If the present tests have any value, it may be as a means to detect gross variations in the reactivity of fly ash from a source that has been proven to be useful by direct tests in concrete mixes.

In summary, most of the standard specifications, though adequate for overall control of fly ash quality, continue to limit properties and require the use of tests that are now understood as largely irrelevant to the behaviour of ash in concrete. On the other hand, relevant properties are not always considered (for example the particle size of ash is ignored in the U.S.S.R. standard) and relevant or best-suited tests are not always required (viz. the use of LOI rather than carbon determination).

Butler (224) has questioned the philosophical basis of the ASTM specification for fly ash in terms that may well be considered in relationship to other national standards.

In essence, he proposes that specified tests for ash should provide for three needs:

- — ensuring that the ash will not be harmful to the desirable properties of concrete;
- — indicating the potential performance of the ash in concrete;
- — monitoring key properties to ensure uniformity.

The first two of these require that ash from a new source be exhaustively examined prior to its introduction into the concrete marketplace, and that regular quality-assurance tests be performed to ensure that ash from a given source remains suitable for use in concrete. Neither of these activities require that testing be performed on every delivered batch of ash.

The third need expresses the requirement for quality control and does demand some routine testing to be applied at the batch level.

9. GENERAL COMMENTS AND RECOMMENDATIONS FOR RESEARCH NEEDS

A great deal of research and field experience on the use of fly ash in concrete has been accumulated and published during the past decade. As a consequence, for reasons both of economy and performance, fly ash is increasingly being considered as a component of concrete, and substantial progress has resulted with regard to its acceptance in construction practice. In particular, it is becoming clear that materials such as high-strength concrete and roller-compacted concrete benefit greatly from the use of fly ash.

It is well established that the problems related to rates of strength development reported during the early years of low-calcium fly ash utilization can now be eliminated. This has been achieved in part by the use of quality-controlled ash and to a substantial extent by the employment of simple changes in the selection of the relative proportions of ash, cement, sand, stone, and water used to make concrete mixes. The use of rational proportioning methods has been shown to produce concretes of any desired strength at ages from 7 to 28 days. When high-calcium fly ashes are used, simple substitution of an equal volume or mass for as much as 20-25% of cement frequently produces concrete that develops strength as rapidly as plain concrete.

A general understanding of the ways in which fly ash influences the rheological properties of fresh concrete is now developing. As a consequence, ash is being used more frequently to aid workability, to supplement other methods of water reduction, and to serve as a component of such specialized products as high-strength and roller-compacted concretes.

In general, experience is revealing that fly ash concrete, when properly proportioned, placed, and cured, is as durable in service as any other concrete.

Research Needs

It is considered that there are at least six aspects of the use of fly ash in concrete that would greatly benefit from more extensive research effort:

- the nature and characteristics of fly ash;
- the properties of fresh concrete;
- the properties of hardened concrete;
- the use of fly ash in conjunction with chemical admixtures and other mineral by-products such as condensed silica fume and ferrous and non-ferrous slags;
- durability;
- specifications and testing.

Understanding the **nature and characteristics of fly ash** is the key to the development of new approaches to its use in concrete, and to the exploitation of the properties of fly ash concrete to the maximum extent. Five issues are of importance in this regard and require considerable research effort:

- the role of particle size distribution in determining the reactivity of ash;
- the determination of the quantity and nature of glass (or other amorphous material) content of fly ash and its influence on ash reactivity;
- the role of chemical composition (especially with respect to minor components such as alkalis and some trace organic components) in determining the reactivity of ash;
- the role of carbon (and the type of carbon) and other components in air-entrainment and the use of chemical admixtures;
- the effects of ash beneficiation on both chemical and physical properties of ash as they influence its performance in concrete.

In many ways the **properties of fresh concrete** are not well understood even in the absence of fly ash. With regard to fly ash concrete, three issues are important:

- set retardation;
- rheology and workability;
- temperature, both from the perspective of the use of ash to control heat generation and, from that, of using heat to influence the reactivity of fly ash as a pozzolan.

The **properties of hardened concrete** are all influenced by the presence of fly ash. In some instances, such as strength development, the effects are well established. Other effects are less well understood; in particular, the influence of fly ash on the following properties requires further examination:

- permeability and porosity;
- creep and shrinkage (especially over extended periods);
- abrasion and erosion resistance.

The use of fly ash and chemical admixtures together, and the co-use of **fly ash with other supplementary cementing materials** such as granulated blast-furnace slag or condensed silica fume, are areas of growing interest that urgently need research. The following items are of immediate concern:

- the effects of fly ash and its components on the activity of such admixtures as air-entraining admixtures, water reducers, and superplasticizers in concrete;
- the effects of condensed silica fume used as a mineral admixture to improve the development of early strength in fly ash concrete;
- the durability of fly ash concretes incorporating other admixtures in severe environments.

The **durability** of fly ash concrete in service is the major facet of fly ash utilization that requires research; in particular, the following aspects of durability are considered to be of urgent concern:

- general aspects of the durability of high-calcium fly ash concretes;
- sulphate resistance;
- durability of roller-compacted air-entrained concrete;
- influence of fly ash on the durability of concretes in marine and other aggressive environments.

The **specifications** for fly ash and its use in concrete, and the tests associated with quality control and compliance, remain unsatisfactory. Tests that have been established to be unreliable or irrelevant persist in specifications, while other means of quality assurance are not accepted. On the one hand, review of specifications with emphasis on performance requirements is urgently needed. On the other, research and development to establish new, more reliable, simpler, and more relevant testing procedures continue to be required to support efforts to improve specifications and codes of practice.

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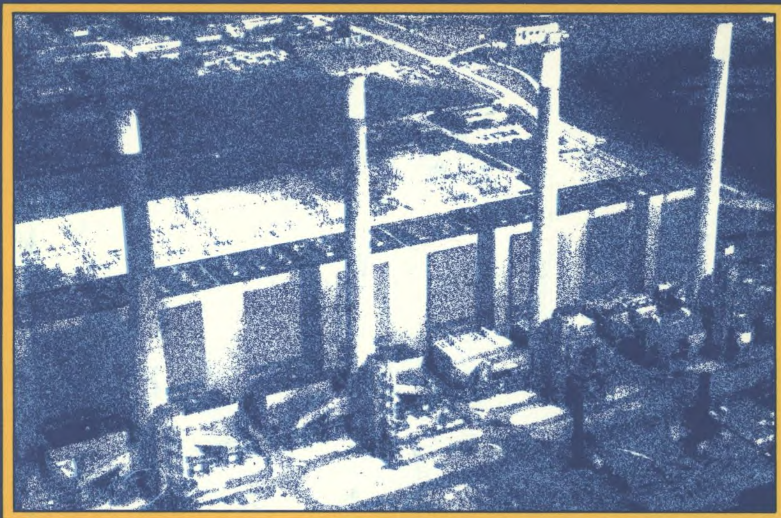

Artist's impression of a coal-burning power plant
Illustration d'une centrale thermique alimentée au charbon

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