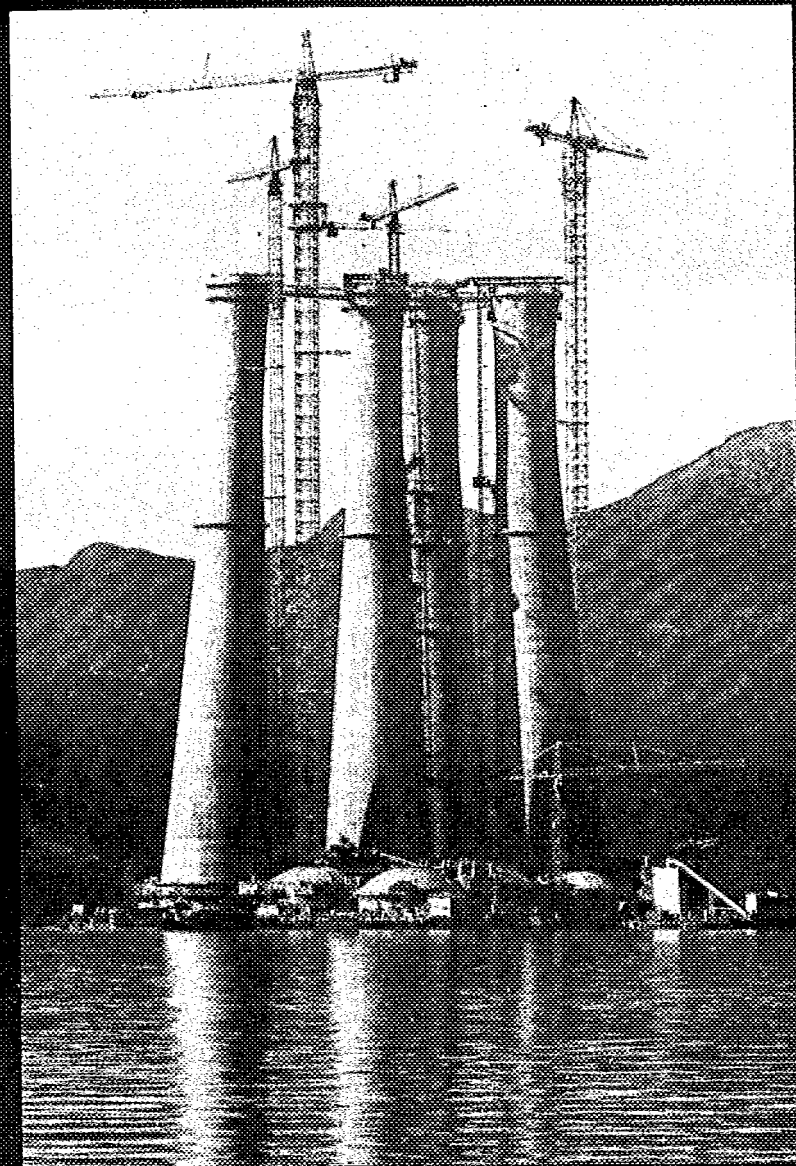


Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete

Proceedings
Third International Conference
Trondheim, Norway, 1989



SP-114
Volume 1



Editor
AAV V. M. Malhotra
Document Sharing Hub

Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete

Proceedings Third International Conference Trondheim, Norway 1989

Volume 1



SP-114

V.M. Malhotra

Editor

American Concrete Institute, Detroit



Documents

Document Sharing Hub

DISCUSSION of individual papers in this symposium may be submitted in accordance with general requirements of the ACI Publication Policy to ACI headquarters at the address given below. Closing date for submission of discussion is December 1, 1989. All discussion approved by the Technical Activities Committee along with closing remarks by the authors will be published in the May-June 1990 issue of either ACI Structural Journal or ACI Materials Journal depending on the subject emphasis of the individual paper.

The Institute is not responsible for the statements or opinions expressed in its publications. Institute publications are not able to, nor intended to, supplant individual training, responsibility, or judgment of the user, or the supplier, of the information presented.

The papers in this volume have been reviewed under Institute publication procedures by individuals expert in the subject areas of the papers.

Copyright © 1989
AMERICAN CONCRETE INSTITUTE
P.O. Box 19150 Redford Station
Detroit, Michigan 48219

All rights reserved including rights of reproduction and use in any form or by any means, including the making of copies by any photo process, or by any electronic or mechanical device, printed or written or oral, or recording for sound or visual reproduction or for use in any knowledge or retrieval system or device, unless permission in writing is obtained from the copyright proprietors.

Printed in the United States of America

Editorial production: Patricia Kost

LIBRARY OF CONGRESS CATALOG CARD NUMBER 89-80361

PREFACE

The Canada Centre for Mineral and Energy Technology (CANMET) of Energy, Mines and Resources Canada, Ottawa, has played a significant role in Canada for over twenty years in research on fly ashes, ferrous and non-ferrous slags, and condensed silica fumes, in order to conserve both resources and energy. In July-August 1983, CANMET in association with the American Concrete Institute and the U.S. Corps of Engineers sponsored a five-day international conference at Montebello, Quebec, Canada, on the Use of Fly Ash, Silica Fume, Slag and Other Mineral By-Products in Concrete. The main purpose of the conference was to bring together representatives from industry, universities, and government agencies to present the latest information on these materials and to explore new areas of needed research. The two-volume proceedings of the conference containing sixty-two papers from fifteen countries were published as ACI Special Publication SP-79.

In 1986, CANMET in association with the American Concrete Institute, the Canadian Society for Civil Engineering, and a number of organizations in Spain sponsored the Second International Conference on the subject of Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete. The conference was held April 21-25, 1986 in Madrid, Spain. The two-volume proceedings of the conference containing seventy-seven papers from more than twenty countries were published as ACI Special Publication SP-91.

In 1989, CANMET in association with the American Concrete Institute, Norwegian Institute of Technology and several other organizations in Canada and Norway sponsored the Third International Conference on the above subject. The conference was held June 18-23, 1989 in Trondheim, Norway. More than 150 papers from 30 countries were received and reviewed in accordance with the policies of the American Concrete Institute; 83 papers were accepted for publication. To all those whose submissions could not be included in the symposium volumes, the Institute and the Conference Organizing Committee extend their appreciation for the interest and hard work. The accepted papers are published in two volumes, the first volume contains papers dealing with fly ash and natural pozzolans, and the second volume consists of papers dealing with condensed silica fume and ferrous and non-ferrous slags. Some papers could have been published in either volume because the material covered more than one subject.

In addition to the papers which have been published in these volumes, more than 60 papers were presented in so-called "research sessions" and as "posters." Some of these papers were published as "supplementary papers", and the authors have been encouraged to publish them in technical journals of their choice.

Thanks are extended to those ACI members and others who helped review manuscripts. Without their prompt review and constructive comments, it would not have been possible to publish these volumes before the conference. The cooperation of the authors in accepting reviewers' suggestions and revising their manuscripts accordingly is greatly appreciated. Particular thanks are extended to Dr. V.S. Ramachandran for his assistance in carrying out extensive editing of a number of submissions.

The help and assistance of Mr. H.S. Wilson, Dr. M. Alasali, and Ms. V. Sivasundaram, all of CANMET, for administrative work associated with this publication is gratefully acknowledged.

V.M. Malhotra, Editor
Chairman, CANMET/ACI
Third International Conference on the Use of Fly Ash,
Silica Fume, Slag and Natural Pozzolans in Concrete

Organizing Committee
Third International Conference
on
The Use of Fly Ash, Silica Fume, Slag
and Natural Pozzolans in Concrete
Trondheim, Norway
1989

V.M. Malhotra
Chairman

H.S. Wilson
Secretary-Treasurer

Members

T.W. Bremner
G.G. Carette
H.L. Isabelle
V.S. Ramachandran

Dedicated to all those ACI members and others
who assisted in the review of the manuscripts

CONTENTS

PREFACE.....	iii
POZZOLANIC AND CEMENTITIOUS BY-PRODUCTS IN CONCRETE -- ANOTHER LOOK by P.K. Mehta.....	1
PROPERTIES OF CONCRETE INCORPORATING LOW QUANTITY OF CEMENT AND HIGH VOLUMES OF LOW-CALCIUM FLY ASH by V. Sivasundaram, G.G. Carette, and V.M. Malhotra.....	45
CHEMICAL MODELLING IN BLENDED CEMENT SYSTEMS by M. Atkins, D.E. Macphee, and F.P. Glasser.....	73
INFLUENCE OF FINENESS OF FLY ASHES ON THEIR HYDRAULIC ACTIVITY by Z. Giergiczny and A. Werynska.....	97
FLY ASH AND SILICA FUME CHEMISTRY AND HYDRATION by D.M. Roy.....	117
PROPERTIES OF CONCRETE CONTAINING LOW-CALCIUM FLY ASH UNDER HOT AND HUMID CLIMATE by R. Sri Ravindrarajah and C.T. Tam.....	139
INFLUENCE OF CURING AT DIFFERENT RELATIVE HUMIDITIES ON THE HYDRATION AND POROSITY OF A PORTLAND/FLY ASH CEMENT PASTE by D.C. Killoh, L.J. Parrott, and R.G. Patel.....	157
EFFECT OF CONDENSED SILICA FUME AND FLY ASH ON COMPRESSIVE STRENGTH DEVELOPMENT OF CONCRETE by M. Ronne.....	175
THE EFFECT OF CURING ON THE STRENGTH AND PERMEABILITY OF PFA CONCRETE by M.D.A. Thomas, J.D. Matthews, and C.A. Haynes.....	191
IMPROVEMENTS IN THE PROPERTIES OF CONCRETE UTILIZING "CLASSIFIED FLY ASH" by K. Ukita, S. Shigematsu, and M. Ishii.....	219
BENEFICIATED FLY ASH: HYDRATION, MICROSTRUCTURE, AND STRENGTH DEVELOPMENT IN PORTLAND CEMENT SYSTEMS by E.E. Berry, R.T. Hemmings, W.S. Langley, and G.G. Carette.....	241
PREDICTION OF CARBONATION DEPTH OF CONCRETE WITH FLY ASH by H. Ohga and S. Nagataki.....	275

PERMEABILITY AND CORROSION RESISTING CHARACTERISTICS OF FLY ASH CONCRETE IN ARABIAN GULF COUNTRIES by O.S.B. Al-Amoudi, Rasheeduzzafar, and M. Maslehuddin.....	295
CARBONATION OF CONCRETE WITH FLY ASH AND CORROSION OF REINFORCEMENTS IN 20-YEARS TESTS by M. Kokubu and S. Nagataki.....	315
TEMPERATURE RISE AND DURABILITY OF CONCRETE CONTAINING FLY ASH by R.S. Barrow, K.M. Hadchiti, P.M. Carrasquillo, and R.L. Carrasquillo.....	331
DEICER SCALING RESISTANCE OF LEAN CONCRETES CONTAINING FLY ASH by D. Whiting.....	349
EFFECTIVE ALKALIS FROM PULVERISED FUEL ASH, GRANULATED BLAST FURNACE SLAG AND NATURAL POZZOLANA DEDUCED FROM MORTAR BAR EXPANSION RESULTS by J.J. Kollek.....	373
STUDY ON THE EFFECT OF THE QUALITY OF FLY ASH FOR CONTROLLING ALKALI-AGGREGATE REACTIONS by S. Kobayashi, Y. Hozumi, T. Nakano, and T. Yanagida.....	403
EFFECTS OF ALKALIES IN CLASS C FLY ASH ON ALKALI-AGGREGATE REACTION by C. Lee.....	417
ALKALI-AGGREGATE REACTION IN CONCRETE: INVESTIGATIONS OF CONCRETE EXPANSION FROM ALKALI CONTRIBUTED BY POZZOLANS OR SLAG by M.M. Alasali.....	431
SHRINKAGE AND CREEP BEHAVIOUR OF HIGH FLY ASH CONTENT CONCRETE by R.N. Swamy and H.B. Mahmud.....	453
COMPARISON OF DIFFERENT METHODS FOR TESTING THE POZZOLANIC ACTIVITY OF FLY ASHES by F. Sybertz.....	477
HYDROTHERMAL REACTIVITY OF RICE HUSK ASH AND ITS USE FOR CALCIUM SILICATE PRODUCTS by N. Hara, H. Yamada, K. Inoue, N. Inoue, S. Tsunematsu, and H. Noma.....	499
PHYSICAL PROPERTIES OF CEMENT PASTE AND CONCRETE CONTAINING PEAT FLY ASH by A. Ipatti.....	517

PROPERTIES OF DIFFERENT TYPES OF CONCRETE CONTAINING PEAT ASH by A. Heikkinen.....	539
THE ACQUISITION AND ANALYSIS OF DATA ON FACTORS AFFECTING THE FIELD PERFORMANCE OF PLAIN AND BLENDED CEMENT CONCRETE STRUCTURES by D. Baweja and H. Roper.....	553
COMPARISON OF CREEP AND SHRINKAGE OF HIGH-STRENGTH SILICA FUME CONCRETES WITH FLY ASH CONCRETES OF SIMILAR STRENGTHS by M.D. Luther and W. Hansen.....	573
APPLICATION OF CONCRETE INCORPORATING BOTH CONDENSED SILICA FUME AND FLY ASH AT FANCUO HYDROPOWER STATION by L. Baoyu, L. Anqi, and X. Pengfei.....	593
72-STORY HIGH-RISE WITH 83 MPa FLY ASH CONCRETE -- A CASE HISTORY by F.D. Anderson.....	607
RAPID CHLORIDE ION PERMEABILITY TEST: DATA ON CONCRETES INCORPORATING SUPPLEMENTARY CEMENTING MATERIALS by P. Plante and A. Bilodeau.....	625
CARBONATION OF PORTLAND BLAST FURNACE SLAG CEMENT CONCRETE WITH FLY ASH by J. Bijen, G. van der Wegen, and R. van Selst.....	645
EFFECT OF FLY ASH AND SLAG ON THE INTERFACIAL ZONE BETWEEN CEMENT AND AGGREGATE by M. Saito and M. Kawamura.....	669
INFLUENCE OF DIFFERENT POZZOLAN TYPES UPON THE EFFECT OF PLASTIFYING ADMIXTURE by P.A. Dahl and I. Meland.....	689
PROPERTIES OF CONCRETES FOR THIN UNDERWATER PLACEMENTS AND REPAIRS by W.T. Hester, K.H. Khayat, and B.C. Gerwick, Jr.....	713
PROPERTIES OF CEMENT PASTE CONTAINING RICE HUSK ASH by C.-L. Hwang and D.-S. Wu.....	733

Pozzolanic and Cementitious By-Products in Concrete—Another Look

by P.K. Mehta

Synopsis: This paper intends to update a previous (1983) critical review by the author on pozzolanic and cementitious by-products for use in concrete. The by-products included in this report are fly ash, granulated blast-furnace slag, and condensed silica fume. Recently available worldwide statistics on production and utilization rates of these mineral admixtures are given. As far as possible new and useful information is presented on their physical and chemical characteristics, structure and reactivity of the glassy phase present, mechanisms by which concrete properties are enhanced, and engineering properties of concrete containing siliceous by-products. A special emphasis is given to durability aspects of concretes incorporating fly ash, blast-furnace slag, or condensed silica fume. Finally, the status of standard specifications and test methods is reviewed, and the contribution of siliceous by-products to make concrete an environment-friendly material of construction is emphasized.

Keywords: admixtures; alkali-aggregate reactions; blast furnace slag; compressive strength; concrete durability; fly ash; glass; microstructure; particle size distribution; reviews; rheological properties; silica fume; specifications; workability

2 Mehta

P. K. Mehta, FACI, is Professor in the Civil Engineering Department at the University of California at Berkeley. He is the author or coauthor of more than 125 technical papers and a book on microstructure and properties of concrete. He is also the recipient of the Wason Medal for Materials Research awarded by the ACI, and a CANMET/ACI award on performance of concrete in marine environment.

INTRODUCTION

In 1983, at the First International Symposium on Fly Ash, Silica Fume, and Slag, the author presented a comprehensive report on pozzolanic and cementitious by-products used in concrete (1). During the last five years a relatively large number of publications dealing with the subject have appeared. For example, the proceedings of the Second Int'l Conference on Fly Ash, Slag, Silica Fume, and Natural Pozzolans (Madrid, 1986) contain 80 papers in a Special Publication of the ACI (SP-91), and the proceedings of the Eighth Int'l Congress on the Chemistry of Cements (Rio de Janeiro, 1986) contains 4 special reports and 43 supplementary reports on the subject. In addition to numerous research papers that are routinely published in scientific and technical journals, the author is aware of at least five books (2-5) and four committee reports (7-10) which attempt to cover the state of the art in a comprehensive manner.

This review is not intended to be a digest of the 1983-87 publications on pozzolanic and cementitious by-products used in concrete. Instead, it is the intention of the author to provide an update on the topics covered by the previous review (1) and highlight any new information which, in the author's view, represents a significant advancement to the state of the art.

First, a brief review of the more recent rates of production and utilization of pozzolanic and cementitious by-products in many countries of the world will be presented. This will be followed by new and useful information on their physical and chemical characteristics, influence on concrete properties, specifications and test methods, and contribution of siliceous by-products in making concrete an environment-friendly material of construction.

PRODUCTION AND UTILIZATION RATES

The 1984 production and utilization rates of fly ash, blast-furnace slag, and condensed silica fume for several countries of the world (Table 1) were compiled by the RILEM Technical Committee 73-SBC, Siliceous By-products in Concrete (10). A comparison between the 1984 and the 1980 statistics (1) shows that in some developed countries, whereas the annual rates of fly ash being produced and used in the cement and concrete industries have remained fairly stable, the corresponding rates for blast-furnace slag and condensed silica fume have dropped

steeply. For instance, during this period the U.S. production of blast-furnace slag has dropped from about 26 million tonnes to 13 million tonnes and condensed silica fume production from about 300,000 tonnes to 100,000 tonnes. This is because the production of these two by-products is related to the steel production which, in the recent years, has come down sharply in the United States.

Although the actual statistics from the U.S.S.R. are not available, it seems that the largest producers of fly ash in the world (with at least 10 million tonnes fly ash production per annum) are the U.S.S.R., U.S.A., China, India, U.K., and South Africa. The fly ash utilization rates by the cement and concrete industries vary from a high of about 20% for China to a low of about 1% for South Africa. In general, poor quality and lack of uniform composition are cited as the primary reasons for low utilization rates of fly ash as a pozzolan. With a better understanding of technical requirements for satisfactory performance of fly ash in concrete, followed by development of proper test methods and specifications, it seems that the utilization rate for fly ash can be much higher than at present.

Japan, China, Germany, USA, and France are among the largest producers of iron blast-furnace slag. Traditionally, a considerable proportion of the total available slag is air-cooled and, therefore, is not as cementitious as the quickly-cooled products (granulated or pelletized slags). The slag utilization rates shown in Table 1 are for the quickly-cooled slag, which is cementitious without excessive grinding. Unlike fly ash, the physical-chemical characteristics of iron blast-furnace slag from a given production facility do not show large variations from one day to another. The availability of a uniform-quality slag is one of the reasons why the rates of slag utilization are much higher than fly ash. For instance, the cement and concrete industries in many countries of the world consume approximately 1/3 to 2/3 of their total iron blast-furnace slag production.

Compared to approximately 1 million tonnes production in 1980 (1), the current world production of condensed silica fume appears to be of the order of 500,000 tonnes, which is considerably less than the total available quantities of fly ash or blast-furnace slag. Due to the highly-pozzolanic characteristics of the material, it is relatively more expensive and therefore its use is limited to special applications, such as for making high strength or high durability concrete mixtures. Specially processed rice husk ash is also highly pozzolanic (1), however at present it is not being produced or used in any significant quantity.

CLASSIFICATION

It is generally accepted now that the cementitious and pozzolanic properties of siliceous by-products used as cement additions depend on their particle characteristics and mineralogical composition, and not on their chemical composition and source of origin. Therefore, in the previous paper (1) the author made an attempt to classify these products on the basis of their cementitious or pozzolanic activity when used in combination with portland cement. Since this classification transcends the traditional barriers according to which the materials are classified by source, a benefit from this approach is the possible development of a single, performance-based, standard specification covering all mineral admixtures. Table 2 shows the revised version of the original classification (1),

4 Mehta

which has recently been approved by the RILEM Technical Committee on the use of siliceous By-products in Concrete (10). According to the classification proposed in Table 2, all siliceous by-products used by the cement and concrete industries can be divided into five categories, which are briefly described as follows:

The **Cementitious** mineral admixtures consist of fine particles of essentially a silicate glass, which has been considerably modified by the presence of large amounts of calcium, magnesium, and aluminum ions. Relatively small amounts of portland cement or other activators (e.g., alkalis or gypsum) are needed to accelerate the hydration and the rate of strength development from this class of mineral admixtures, to which rapidly-cooled blastfurnace slag and some high-calcium fly ashes (> 20% CaO) belong.

As will be discussed later, the composition of the silicate glass in some industrial by-products may not be uniform. It is possible that a part of the glass is essentially an aluminosilicate glass whereas the remainder is a silicate glass containing large amounts of calcium and magnesium. In such a case, the product will be partly cementitious and partly pozzolanic. The high-calcium fly ashes, with 10 to 20% CaO, are categorized as **cementitious** and **pozzolanic** mineral admixtures.

By-product materials which consists mostly of a silicate glass, modified with aluminum and iron, are categorized as **normal pozzolans**. Compared to the calcium-magnesium substituted silicate glass, the aluminum-iron substituted glass appears to be less reactive. The low-calcium fly ashes containing this type of glass are categorized as normal pozzolans.

By-products, which consist essentially of silica in a non-crystalline and high surface-area form, exhibit great pozzolanic activity and are therefore categorized as **highly pozzolanic**. Condensed silica fume and specially processed rice husk ash belong to this category.

The last category contains mineral admixtures of low reactivity, such as slowly-cooled blastfurnace slag and bottom ash, which must be pulverized to very fine particle size in order to develop acceptable levels of strength in combination with portland cement.

PHYSICAL AND CHEMICAL CHARACTERISTICS

A summary of typical physical and chemical characteristics of the principal by-products used as mineral admixtures in concrete is presented in Table 2. It is the particle shape and size distribution as well as the mineralogical composition of a mineral admixture, including the types and amounts of both crystalline and non-crystalline (amorphous or glassy) phases present, which affect concrete behavior. It would therefore be useful here to compare the similarities and differences in physical and chemical characteristics of fly ash, granulated blast-furnace slag, and condensed silica fume. Particular attention should be paid to the nature of glass in fly ash because, since the previous review (1), some valuable information has recently become available on this subject.

Particle Characteristics

Fly ash is a condensation product from droplets of molten coal ash, and is therefore mostly spheroidal, with individual particles ranging from less than 1 μm to greater than 1 mm. Condensed silica fume is formed by condensation of silicon oxide vapor, and the particles are also spheroidal. However it is a much finer material than other mineral admixtures, with grain size distribution in the 0.02 to 0.3 μm range. The most commonly used method of rapid cooling of slag is by water granulation. The molten slag is broken up by high-pressure water jets to sand-size grains, which are subsequently dried and mechanically pulverized to < 45 μm particles (passing No. 325 mesh sieve).

Using X-ray sedimentation technique, particle size distribution data for several U.S. fly ashes was reported by Mehta (11). In general, probably due to the presence of larger amounts of alkali sulfates, the high-calcium fly ashes tend to be finer than the low-calcium fly ashes. This study showed the possibility of a relationship between the amount of < 10 μm particles in fly ash and the 7 or 28-d compressive strength of blended cements containing fly ash. Similarly, using electron microscopy, particle size distribution plots for several types of condensed silica fume are reported by Aitcin et. al (12). Condensed silica fume from silicon metal manufacture is usually finer because of the higher furnace temperature. With ferrosilicon alloy furnaces, as the amount of iron increases in the alloy, the temperature of the furnace decreases and the grain size distribution of the condensed silica fume tends to shift toward coarser particles. Like fly ash, the observed difference in the reactivity of different types of silica fume can, to some extent, be related to the size distribution of particles (6).

Typical nitrogen adsorption surface areas for fly ash, ground granulated blast-furnace slag, and condensed silica fume are on the order of 300 to 500 m^2/kg , 400 to 600 m^2/kg , and 17,000 to 20,000 m^2/kg , respectively.

The physical characteristics of siliceous by-products account for their water-reducing ability in portland cement concrete mixtures. The vitreous (glass), smooth, and non-absorbing surface texture of these admixtures is in part responsible for better workability and lower water requirement of pastes, mortars, and concretes containing siliceous by-products as cement replacement. Another reason seems to be the reduction in the volume of voids that is made possible by a denser packing, when fine spherical particles are present in a concrete mixture. Helmuth (13) believes that the water reduction in portland cement-fly ash mixtures is the result of a better dispersion of cement particles. Very small fly ash particles get adsorbed on the surface of electrically charged cement grains, causing dispersion of the system in a manner similar to conventional (organic) water-reducing admixtures.

Chemical Characteristics

From numerous publications including the previous review (1), the wide variations in the oxide analyses of siliceous by-products become readily apparent. In the U.S. typical chemical analyses for low-calcium fly ashes (< 10% CaO), usually formed by combustion of bituminous coal, show 45-65% SiO_2 , 20-30% Al_2O_3 , 4-20% Fe_2O_3 , 1-2% MgO, up to 3% alkalis, and up to 5% loss on ignition (9,11). The high-calcium fly ashes (> 10% CaO) formed by combustion of

6 Mehta

subbituminous and lignite coal, typically contain 20-50% SiO_2 , 15-20% Al_2O_3 , 15-30% CaO , 5-10% Fe_2O_3 , 3-5% MgO , up to 8% alkalis, and less than 1% loss on ignition. The chemical composition range for iron blast-furnace slag produced in the U.S. and Canada (5,8) corresponds to 32-40% SiO_2 , 7-17% Al_2O_3 , 29-42% CaO , 8-19% MgO , and up to 2% each sulfur and iron oxide. The condensed silica fume from Si and FeSi-75% industries shows a relatively narrow chemical composition range (6,7,12) which, typically, corresponds to 90-95 SiO_2 , 0.3 to 0.7% Al_2O_3 , 0.1 to 3% Fe_2O_3 , 0.1 to 0.5% MgO , 0.1 to 1% CaO , up to 1% alkalis, and up to 4% loss on ignition.

It is generally accepted that there is **little correlation between the oxide analysis of a mineral admixture and its performance in concrete**. From the standpoint of concrete behavior, the chemical composition is important only to the extent that it influences the mineralogical characteristics of the mineral admixture, including the glass content and type. In addition to chemical composition, the processing conditions also influence the mineralogical characteristics of the product. Therefore, variations in processing parameters in industrial furnaces make it possible that two samples of fly ash, with a similar chemical analysis, would give entirely different mineralogical compositions and performance characteristics in concrete.

Although the crystalline components present in some mineral admixtures have the ability to affect properties of concrete, it should be noted that most of them are inert or poorly reactive to water. The predominant constituent in fly ash, granulated blast-furnace slag, and condensed silica fume is the, non-crystalline (amorphous), silicate glass. There is a growing realization among the researchers now that the key to differences in reactivity (for instance, between two fly ashes or two slags, or between a fly ash and a slag) has to be sought in the characteristics of the glass present.

The **crystalline minerals** in low-calcium fly ashes generally comprise of quartz, mullite, and magnetite or ferrite spinel. In addition to quartz, the crystalline phases in subbituminous fly ashes are known to include C_3A , $\text{C}_4\text{A}_3\bar{\text{S}}$, calcium sulfate, and alkali sulfates. The calcium compounds and alkali sulfates are reactive. In fact, some fly ashes with large proportions of C_3A or free CaO are known to cause quick setting and high heat of hydration, but such fly ashes are exceptions rather than the rule. The crystalline compounds identified in devitrified blast-furnace slags (1,5) are mainly the melilite solid solution series with end members gehlinite (C_2AS) and akermanite (C_2MS), and lesser amounts of monticellite (CMS), diopside (MCS_2), and merwinite (C_3MS_2).

Typically, fly ashes contain 60 to 90% glass, granulated slags contain 85-95% glass, and condensed silica fume consists essentially of vitrified silica (100% glass). The characteristics of the glassy phase in siliceous by-products, which range from simple (condensed silica fume) to highly complex (fly ashes), are discussed next. It will also be helpful here to include a brief description about the structure of glass, which is based on a review by Hemmings and Berry (14).

Structure of Glass

Solid materials lacking long-range interatomic order are generally non-crystalline. Among these, glasses form a special group that can best be

described as, "the product of fusion of inorganic materials, which have cooled to a rigid condition without crystallizing". The degree of disorder in a glass can be inferred by observations of the way in which it diffracts X-rays to form a diffraction pattern. Fig. 1 illustrates diffraction patterns of: (a) ordered, crystalline SiO_2 (cristobalite); and (b) non-crystalline SiO_2 . In the non-crystalline state, diffraction of X-rays results in a broad diffuse halo rather than sharp diffraction peaks.

Further, according to Hemmings and Berry (14), a feature of simple glass-forming oxides, such as pure SiO_2 , is that although the integral structure lacks long-range order, there is continuity in the chains of constituent atoms (Fig. 2a). The disorder results from randomness in the size of the rings into which these chains are linked to form a structural network. When more complex glasses are formed, for example by introducing sodium ions into the silicate structure, a greater level of disorder results. Not only are the rings of the glass-forming component disordered, but also many are broken to form non-bridging oxygen atoms (Fig. 2b). As more constituents are introduced into a glass, further levels of disorder result, e.g., random chemical disorder may be caused by the replacement of Si by Al or Fe (Fig. 2c). Most of the glasses of practical interest to the cement industry are disordered both by chain breaking through the presence of modifier cations such as Na, K, and Ca, and by chemical disordering of the chains (Al, Fe).

Glass in condensed silica fume--X-ray diffractograms of samples of different types of condensed silica fume shown in Fig. 3a (6) reveal that the material is essentially vitreous silica with a diffuse halo peak at about $4.4\text{\AA}$ ($21.9^\circ 2\theta_{\text{max}}$, Cu $K\alpha$). This happens to be the strongest peak for cristobalite. In fact, when heated to 1100°C and subsequently cooled slowly, condensed silica fume will form crystalline cristobalite (Fig. 1a).

Glass in rapidly cooled blast-furnace slag--X-ray diffractograms of three quenched blast-furnace slag samples are shown in Fig. 3b (14). The predominant halo with $2\theta_{\text{max}}$ at about 32° , clearly indicates their essentially non-crystalline composition, with minor amounts of crystalline components present (melilite, merwinite, and quartz). It should be noted that in the previous review the author (1), on the basis of the diffuse halo peaks on diffractograms, was able to point out the similarity in the composition of glass between a granulated blast-furnace slag and a high-calcium fly ash.

Glass in fly ash--Since glass is the major component of fly ashes, the impetus for research on composition of glass in fly ash came from the general observation that low-calcium fly ash is less reactive than high-calcium fly ash. On the basis of the position of the diffraction halo produced by X-ray scattering, Diamond and Lopez-Flores (15) as well as this author (1) pointed out that the composition of glass is different in low-calcium and high-calcium fly ashes. Typically, low-calcium fly ashes show a diffuse halo maxima at $21\text{--}25^\circ 2\theta$ (Cu $K\alpha$), and high-calcium fly ashes at $30\text{--}34^\circ 2\theta$.

From similarities in the X-ray diffraction diffuse halo maxima between high-calcium fly ash and granulated blast-furnace slag, this author (1) speculated that the composition of the glass in high-calcium fly ash is essentially melilitic, i.e. a silicate glass modified with calcium and aluminum. On the other hand,

8 Mehta

Diamond (16) attributed the $32^\circ 2\theta$ diffraction halo from glass in high-calcium fly ashes ($> 20\%$ CaO) to a calcium aluminate type glass, similar to $C_{12}A_7$. Recent reports of work by Roode (17) and Hemmings and Berry (18), as will be discussed next, support the conclusion reached by this author (1).

There is no doubt that the value of $2\theta_{\max}$ on a typical XRD pattern for fly ash indicates the extent of glass modification. Diamond (16) concluded that with increasing calcium content of fly ash in the zero to 20% analytical CaO range, the value of $2\theta_{\max}$ increased gradually from about 22° to $28^\circ 2\theta$; however with high-calcium ashes (20–30% CaO) the $2\theta_{\max}$ shifted to $32^\circ 2\theta$ (Fig. 4). Diamond attributed $32^\circ 2\theta_{\max}$ to a calcium aluminate type glass similar in composition to $C_{12}A_7$. Other researchers including McCarthy et. al (19), Roode and Hemmings (17), and Mehta (20), working with a broad base of fly ashes, confirmed the general trend of increase in the $2\theta_{\max}$ value with increasing CaO in fly ash but could not confirm the discontinuity in the CaO vs $2\theta_{\max}$ plot as reported by Diamond (Fig. 4). Whereas the interpretation vis-a-vis $C_{12}A_7$ glass remains in doubt, there is little doubt from the XRD data of fly ashes that the composition of the silicate glass is modified by substitution with other ions, such as Al, Ca, Mg, Fe, Na, and K.

Hemmings and Berry (18) have presented an excellent overview of the state-of-the-art on the nature of glass in fly ash. The authors attempted to resolve two important issues which have a direct bearing on the relationship between the composition of fly ash and its reactivity. To address the question: is the value of $2\theta_{\max}$ an indication of the extent of glass modification, the work of Roode and Hemmings (17) is cited. The authors examined sodium silicate model glasses in which sodium content varied from zero to 50% (Table 3). In these systems, the ratios between non-bridging oxygens to silicon ranged from zero to 2, with structures that became progressively more depolymerized (i.e. network $>$ sheets $>$ chains $>$ monomer). From the corresponding XRD patterns (Fig. 5), it can be observed that there is a marked shift in the halo to the higher $2\theta_{\max}$ with increasing Na_2O content. It should be noted that the halo shows at least two maxima of varying intensity: a low-angle composition at $22\text{--}24^\circ 2\theta_{\max}$ and a high-angle composition at $30\text{--}34^\circ 2\theta_{\max}$. Therefore, Roode and Hemmings (17) concluded that, even in simple systems, different glass types can co-exist over a wide range of compositions (i.e. they are phase separated, and are distinguishable by their XRD patterns). Hemmings and Berry (18) point out the significance of this investigation to fly ash systems. The implications are that if the fly ash halo is asymmetric and shifts in position, it may be attributable to any or all of the following: (a) different glass with different modifier levels in different particles (inter-particle speciation), (b) different glasses in the same particle (intra-particle speciation), or (c) phase separation.

Hemmings and Berry (18) investigated the extent of inter-particle differences in fly ash glass by examining ash fractions separated by density. Density-separated fly ash fractions exhibited not only dramatic changes in bulk chemical composition but also in their XRD patterns. It was shown that the $2\theta_{\max}$ values of the diffuse halos of these fractions correlated strongly with the total network modifier cation contents of the glasses. Thus, the authors concluded that different glass types co-existed within samples of fly ash from a single source, and therefore the asymmetry of the glass halo in the bulk ash is caused by an overlap in the XRD patterns of the constituent glasses. The authors also concluded

that the shift in the XRD halo to higher $2\theta_{\max}$ values for different size fractions of a fly ash is the result of an increasing content of cation modifiers in essentially the same aluminosilicate matrix (and not due to formation of a new type of glass, viz, $C_{12}A_7$ glass).

REACTIVITY

In solids, a close relationship exists between the microstructure of a material and its properties. The microstructure of hydraulic cement products is influenced by the hydration reactions of various constituent phases, both crystalline and non-crystalline, under given curing conditions. The previous paper (1) contains a comprehensive review of the physical-chemical changes associated with the hydration of portland cement minerals, and relative rates of reactivity of various siliceous by-products when used in combination with portland cement. Briefly, it was shown that portland cement consists essentially of highly reactive crystalline minerals, which hydrate under ambient curing conditions to form a relatively porous solid with a heterogeneous structure composed mainly of calcium silicate hydrates (CaO/SiO_2 ratio, approximately 1.5), calcium hydroxide, and calcium sulfoaluminate hydrates.

The pozzolanic and cementitious by-products consist essentially of non-crystalline matter,* which, under ambient conditions hydrates slowly even in the presence of the alkaline solution that is formed by the dissolution of portland cement minerals. The reason for the slow reactivity is the mechanism of hydration according to which the particles of mineral admixtures hydrate essentially in situ by diffusion controlled reactions, as will be discussed. This is why particle size or surface area plays a dominant role in determining the relative rates of reactivity. For instance, it was stated that condensed silica fume which, typically, has extremely fine particle size ($0.1 - 0.3 \mu m$) compared to the average particles in slag or fly ash ($10-20 \mu m$), begins to contribute to the strength of portland cement mortar or concrete after 1-d curing, whereas slags take more than 3 days, and fly ashes more than 7 to 14 days (1).

The relative rates of hydration of pozzolanic and cementitious materials depend, in general, on their particle size and composition of the non-crystalline phase, both of which control the activation energy available for the hydration reactions. The concept of activation energy involves chemical energy from the chemical reactants (i.e., chemical composition of the non-crystalline phase and the solution chemistry of the contact fluid), mechanical energy from fine grinding, and thermal energy from heat of hydration or an outside heat source (21). Important findings on reactivity, hydration reactions, and microstructure of blended portland cements containing various pozzolanic and cementitious admixtures are summarized next.

*exception to this, as discussed earlier, are some high-calcium fly ashes containing crystalline minerals, such as C_3A and $C_4A_3\bar{S}$, which are reactive.

10 Mehta

According to Hooton (22), factors affecting the slag reactivity (hydraulicity) are the degree of vitrification (glass content), the chemical composition, the fineness of grinding, and the activation of slag glasses by chemical or thermal means. Although increasing glass devitrification (crystallization) reduces the reactivity of a slag, the relationship between the glass content of slag and the strength development in a blended portland cement containing the slag is not linear. In fact Demoulian et al. (23), and more recently Frearson and Uren (24), have reported that the presence of some crystalline merwinite in certain slag glasses made them more reactive.

Although the non-crystalline structure (glassy state) is essential to the slag reactivity, the chemical composition of slag is also a factor. For instance, it is generally known that commercial high SiO_2 glasses are not readily attacked by water or alkaline solutions, but their reactivity increases with increasing content of CaO , MgO , and Al_2O_3 . In fact a basicity factor, $(\text{C}+\text{M}+\text{A})/\text{S} \geq 1.0$, is used in Germany to evaluate the quality of slag for use in blended cements. Also, in his review Hooton (22) cites Kondo's work showing that iron blast-furnace slag is both cementitious and pozzolanic. For instance, to develop high levels of strength, some Japanese slags require more calcium hydroxide than is needed for glass activation alone.

Compared to hydrated portland cement, a similar slag-cement paste (with identical water/cement ratio and curing conditions) will have a denser microstructure and a relatively lower calcium hydroxide content. Many investigators including this author (1), have reported that in normally-cured cement pastes the inclusion of slag shifts the pore size distribution from coarser to finer pores. Since the presence of large capillary pores is believed to be responsible for high permeability and low strength of a hardened cement paste, this physical modification of the microstructure rather than any chemical modification seems to play a more important role in improving the strength and durability of slag-cement products.

Recently, Harrison et al. (25) reported the microstructure of hydrated cement pastes containing 40% slag. Reaction rims around slag particles and relics of fully reacted slag particles demonstrated that the slag hydration reactions were diffusion-controlled. Qualitatively, the microstructure resembled neat portland cement pastes of similar ages except that less $\text{Ca}(\text{OH})_2$ was present, and the composition of the C-S-H in fully reacted slag particles corresponded to a Si/Ca ratio of 0.62.

As with iron blast-furnace slag, the reactivity of fly ash in portland cement-fly ash mixture depends largely on dissolution of the glassy structure by the hydroxide ions present as a result of the portland cement hydration. Again, many researchers including this author (20), have shown that the reactivity of fly ash is greatly influenced by the curing temperature and the fineness of fly ash. Portland cement-fly ash mixtures made with several U.S., low-calcium or high-calcium fly ashes, when cured at 50°C , produced similar levels of strength in 7 days as normally cured (20°C) mixtures in 28 days. Under most ambient conditions, massive concrete members can easily attain temperatures of the order of 50°C due to the heat evolved during the hydration of portland cement. Also, from the data on the particle size distribution of fly ashes, the author (20) concluded that fly ash particles smaller than $10\text{ }\mu\text{m}$ have a positive influence on

early strength development rates of portland cement-fly ash mixtures.

Again, as with blast-furnace slag, it seems that the hydration of fly ash in the presence of portland cement involves a three-stage reaction. Immediately after mixing with water, reaction rims of impermeable coatings surround the fly ash particles. No further reactions occur until alkali or calcium hydroxide and sulfates ions in sufficient concentration are available in the solution phase. Thus during the second stage, it is primarily the hydroxide ions which activate the hydration of glasses in fly ash. The third and the main reaction involving fly ash hydration is the slow pozzolanic reaction, which continues to consume calcium hydroxide and form calcium silicate hydrates as long as calcium and hydroxyl ions are available.

In regard to the reactivity of condensed silica fume, Cheng-yi and Feldman (27) compared the amount of calcium hydroxide formed at different times during the first three days of hydration in portland cement pastes, both with and without silica fume (30% by weight). For control purposes, a third cement containing 30% of a coarsely ground silica powder was included in the study. The amount of $\text{Ca}(\text{OH})_2$ in the three cement pastes was similar up to 8 hr, however, at later periods, the cement pastes containing no additive showed higher $\text{Ca}(\text{OH})_2$ contents. Subsequently, the paste containing the silica fume showed the lowest calcium hydroxide content because due to the high surface area and noncrystalline nature of silica, the additive in this paste was more pozzolanic than the additive consisting of coarsely ground silica.

Again, as with the hydrated cement pastes containing slag or fly ash, the main characteristics of the microstructure of cement pastes containing 30% condensed silica fume are a dense structure free from large pores and absence of crystalline calcium hydroxide. Mehta and Gjorv (28) determined pore size distributions for various blended cement pastes at a given W/C and hydration ages of 7, 28, and 90 days. The threshold pore diameter (the minimum pore diameter in a solid at which a continuous pore system exists) decreased with silica fume addition even after 7 days of hydration. After 90 days, the threshold diameters decreased in the following order: portland cement > portland cement + fly ash > portland cement + fly ash + silica fume > portland cement + silica fume. Earlier the author had reported a close relationship between the threshold diameter and the permeability in hardened cement pastes. Sellevold and Nilson (29), citing the work by Sellevold et al. and other investigators confirmed that, at a constant W/C, increasing the content of silica fume in concrete leads to the refinement of the pore structure. Feldman (30) showed that a relatively discontinuous system of fine pores exists in hydrated cement pastes containing silica fume.

Kaizaki et. al (31) reported the microstructure of a low W/C ratio (0.25) paste obtained by hydration of a blended portland cement containing 20% condensed silica fume (with 2% superplasticizer by weight of cement). The hardened paste contained a large number of unreacted cement particles surrounded by C-S-H of low Ca/Si ratio (0.67-1.1). In addition to being the source of $\text{Ca}(\text{OH})_2$ supply for the pozzolanic reaction, the cement particles appeared to serve as a filler (microaggregate). The authors confirmed that, compared to hydrated portland cement pastes, the pastes with silica fume contained finer and more discontinuous pores.

12 Mehta

Alkali Activation of Slag

It has been observed that within a few minutes of exposure to water, coatings of aluminosilicate hydrates form on the surface of slag grains. These coatings are impermeable to water and their formation inhibits further hydration unless a **chemical activator** is present. In the presence of a chemical activator the impermeable coating will disintegrate, exposing the slag particle to further hydration. Since hydroxyl or sulfate ions are able to decompose the aluminosilicate-hydrate coating, a portland cement, especially one with more than normal amounts of C_3S , SO_3 , and alkalis, usually can serve as an inexpensive chemical activator for granulated blast-furnace slag.

Since 1970's, instead of portland cement, the alkali activation of slag by the use of sodium or potassium hydroxide, carbonate, sulfate, and silicate has been intensively investigated with mixed results. In Finland, an activator called F-admixture was developed in the late seventies. It consists of a mixture of NaOH, Na_2CO_3 , and a water-reducing admixture (a lignosulfonate). Many researchers have reported studies on the properties of alkali-activated slags. Typical results are given by a recently reported Swedish study using a slag ground to 350, 530, or 670 m^2/kg specific surface. Andersson and Gram (32) tested both normally cured (room temperature curing) and steam-cured (up to 80°) mortars containing the slag, a fine aggregate, and water in the ratio of 1:3:0.43 by weight. The amount of the activator was varied between 3 and 11% by wt. of cement, and air-curing rather than moist-curing was used. At room temperature, with the 530 m^2/kg slag, compressive strengths up to 55 MPa at 28-d were obtained with 6% sodium silicate addition. The strength development with NaOH seemed to be little affected by varying the amounts of NaOH. With steam curing, 56 MPa was achieved in 8 hours only with a 11% sodium silicate activator. Also, in general the higher the amount of alkali activator, the higher was the compressive strength.

Although the strength development was satisfactory, Andersson and Gram (32) found that the drying shrinkage of the air-cured slag mortar was more than double, when compared to the corresponding portland cement mortar. Large autogenous shrinkage on hydration of slag was responsible for extensive microcracking in the system, thus reducing impermeability and durability.

MECHANISMS BY WHICH MINERAL ADMIXTURES IMPROVE CONCRETE PROPERTIES

In the previous report (1) it was emphasized that the incorporation of mineral admixtures in concrete (whether in the form of additions to cement or as admixtures to concrete) would lead to a general enhancement in most properties of concrete, provided the processes by which the properties improve are clearly understood, and a conscious effort is made in the concreting practice to promote these processes.

The processes by which mineral admixtures are able to improve the **rheological behavior of freshly mixed concrete** (viz., consistency, cohesiveness, and reduction in bleeding and segregation), and the **engineering properties of hardened concrete** (strength, elastic modulus, impermeability, and general

durability) are both physical and physical-chemical.

The physical processes depend mainly on the particle size distribution of solids in a concrete mixture. Assuming a minimum cement content, since reduction in voids and water content of a concrete mixture are the key to improvement in many properties, one way to achieve this effect is to densely pack very fine particles of a mineral admixture between the larger particles of the fine aggregate and portland cement. A reduction in both the water content and the size of void spacings in a freshly placed concrete mixture would obviously be accompanied by a significant reduction in bleeding and segregation.

It may be noted that the rate of water flow in a channel is proportional to the square of the diameter of the channel. To reduce the size of channels of flow of bleed water in a concrete mixture, it is necessary that the fine particles of both cement and mineral additive are well dispersed in the concrete mixture. The presence of unsatisfied electrical charges on the surface of portland cement grains is responsible for their flocculating tendency in a cement-water suspension, and the art of deflocculation of cement-water mixtures by the application of plasticizing surfactants is now widely known and practiced in concrete technology. In this regard Helmuth's (13) finding is significant that, like conventional dispersing agents, the particles of fly ash have the ability to disperse a flocculated cement-water system and therefore will act as a water-reducer. Incidentally, this underscores the difficulty of dividing the mechanisms into purely physical or chemical because, in practice, no such separation exists.

With varying degree of effectiveness other mineral admixtures may also act as cement dispersants. Of course depending on the amount used and the particle size characteristics, some mineral additives, such as condensed silica fume, would themselves require the application of powerful dispersants.

In conclusion, for the benefits to be realized from the small particle size of a mineral additive, the mere inclusion of the additive into a concrete mixture is not enough. The additive must be well dispersed, with or without the aid of a conventional plasticizing agent, and by thorough mixing of concrete. In fact, as discussed next, the effectiveness of physical-chemical processes of pore refinement* and grain refinement associated with the hydration reactions of mineral admixtures, which are important in strengthening the microstructure and therefore the engineering properties of concrete, will be largely dependent on a uniform distribution of the fine particles of a mineral admixture throughout the concrete mixture.

The physical and chemical processes responsible for improving the engineering properties of hardened concrete are slow and therefore take a long time to manifest. In the previous review (1) two such processes were highlighted: (a) the presence of very fine particles of a mineral additive not only cause an acceleration of cement hydration reactions but also pore refinement, (b) the

*The term, pore refinement, refers to the transformation of a system containing larger pores into one with smaller pores. The term, grain refinement, refers to the transformation of a system containing larger crystals, such as of calcium hydroxide, into one with smaller crystals (33).

14 Mehta

hydration reactions of pozzolanic and cementitious additives lead to further pore refinement, and also to grain refinement in the hydrated cement paste as well as in the transition zone, which exists between the cement paste and coarse aggregate in concrete. New information is presented here to show that both the processes play an important role in improving the strength and other related properties of concrete.

In a recent experimental study (34), the compressive strength and microstructural characteristics of a high-strength concrete mixture (929 lb/yd³ cement content, 0.35 W/C), both with and without mineral additions, were examined. The mineral additions (10% cement replacement by wt.) consisted of a condensed silica fume (0.1 μm avg. particle size, 20 m²/g surface area), a rice hull ash (50 m²/g surface area), and two ultrafine but non-pozzolanic powders (colloidal carbons with 0.01 and 0.03 μm avg. particle size, and 90 and 36 m²/g surface area, respectively). From the concrete strength data (Fig. 6), and microstructural studies it was concluded that, through pore refinement and grain refinement, mineral additives with ultrafine particle size or very high specific surface (even the non-pozzolanic ones such as colloidal carbon) were able to cause substantial strength improvement in concrete at early ages up to 7 days. In the case of the pozzolanic admixtures, the pozzolanic reaction seems to cause a further improvement in the strength of the cement paste especially in the transition zone, as seen by a steady increase in the concrete strength during the 7 to 28-d hydration period.

Earlier work by Monteiro and Mehta using a condensed silica fume (35), and by Detwiler et al. using a ground granulated blast-furnace slag (36), confirmed that the processes of pore refinement and grain refinement play an important role in improving the strength of the cement paste in the transition zone in concrete. Since the transition zone characteristics seem to govern most of the important properties of concrete, such as strength, elastic modulus, and permeability, it is the opinion of this author (37) that beneficial effects of a pozzolanic or cementitious additive to portland cement cannot be fully demonstrated by determining its influence on the engineering properties of cement pastes and mortars. Since it is the transition zone in concrete that seems to derive the most benefit, direct tests with concrete mixtures are necessary to assess the effect of the mineral admixture on the transition zone characteristics in concrete.

Also, it is concluded that, in addition to the physical densification effect derived from the inclusion of very fine particles in a concrete mixture, the chemical effects associated with the hydration reactions of pozzolanic and cementitious additives are equally important in determining the ultimate engineering properties of concrete. Some researchers seem to think that the chemical effects are not so important. If this was true, there would be no effect of curing temperature on the ultimate strength characteristics of concrete. The ultimate strength of neat portland cement concrete seems to suffer at high curing temperatures (viz, 120 to 150°F). However, with the incorporation of a pozzolan, such as fly ash, the ultimate strength is considerably enhanced. This is mainly because the pozzolanic reaction follows Arrhenius law of the interdependence of curing temperature and the rate of reaction, i.e., an increase in the curing temperature causes more than a proportional increase in the reaction rate (9). Conversely, strength reduction at early ages is expected with concrete containing mineral admixtures when cured at temperatures less than normal (< 70°F). There

is little doubt from research as well as from field experience that the influence of the curing environment* on the diffusion-controlled hydration reactions of mineral admixtures must be paid a much closer attention in concrete containing mineral admixtures than ordinary portland cement concrete without these admixtures.

PROPERTIES OF CONCRETE CONTAINING MINERAL ADMIXTURES

The beneficial effects of mineral admixtures on rheological properties of freshly-mixed concrete and engineering properties of hardened concrete can be anticipated from the above discussion on mechanisms by which mineral admixtures improve concrete properties. In the previous paper (1), many of the technical benefits were reviewed; to emphasize the contribution of by-product admixtures to concrete, as far as possible, only new data on important properties of concrete are presented here. The information presented below will show again that it is the mineralogical and granulometric characteristics of a mineral admixture, and not its source or origin, which control the behavior of concrete.

Workability--The workability and pumpability of a concrete mixture is enhanced by decreasing the friction between aggregate particles. This is generally achieved by increasing the paste content of the mixture. Also, in order to prevent bleeding and segregation the paste should produce a cohesive concrete mixture. In the absence of satisfactory test methods, there is little scientific data in the published literature on the degree of improvement attainable in workability or pumpability of fresh concrete by incorporating mineral admixtures of different physical-chemical characteristics. However, there is general agreement that a combination of factors, as discussed next, leads to a general improvement in the rheological properties of concrete.

First, the incorporation of a mineral admixture, as a partial cement replacement by weight, results in an increase in the volume of the paste in concrete. This is because the density of mineral admixtures is significantly lower than ordinary portland cement. Second, all by-product mineral admixtures, such as fly ash, ground slag, and condensed silica fume consist of fine particles of a glassy (non-absorptive) nature. Third, as discussed before, the introduction of any fines in a concrete mixture tends to reduce bleeding by obstructing the channels of bleed-water flow. Fourth, there is now evidence of the water-reducing ability of mineral admixtures as they tend to disperse the flocculated particles of cement in a freshly made cement paste. Specific examples of how fly ashes, ground slag, and condensed silica fume generally affect slump, workability, bleeding and other characteristics of fresh concrete are found in three recent reports published by the ACI (7,8,9).

*The curing environment not only includes the temperature and humidity but also the ionic composition of liquid phase in concrete, which is mainly determined by the characteristics of portland cement and admixtures used.

16 Mehta

Strength--Recent data regarding the influence of various mineral admixtures on both the ultimate compressive strength and the rate of strength gain in concrete mixtures are generally consistent with the trends described in the previous paper (1).

Briefly, both the ultimate strength and the rate of strength gain depend on the amount and the characteristics of the mineral admixture (viz., particle size distribution or surface area, and the amount and reactivity of glassy phase), the composition of the concrete mixture (viz., cement content and type, water/cement ratio, and the presence of other admixtures), and curing conditions (viz., concrete temperature and environmental humidity). Condensed silica fume and rice husk ashes with very high content of non-crystalline silica and high surface areas (20,000 to 60,000 m²/g) are able to make some contribution to the strength of a given concrete mixture even at very early ages of hydration (viz., 1 to 3-d), significant contribution during the first 2-4 weeks, and relatively little contribution thereafter. Fly ashes and ground blast-furnace slag, with their much coarser particle size distribution and low specific surface (typically 300 to 500 m²/kg), make little strength contribution at very early ages (up to 3 days), some contribution during the intermediate period (3 to 14 days), and considerable contribution thereafter. With finer particle size and increasing calcium content, granulated blast-furnace slags and high-calcium fly ashes usually tend to accelerate the rate of strength gain. It is not possible here to summarize the large number of recent reports containing results of studies on the effect of mineral admixtures on concrete strength; only selected papers are discussed next.

Carette and Malhotra (38) confirmed the general approach suggested by Mehta and Gjorv (28) that the problem of low early-age strength with concretes containing fly ash can be overcome by using both fly ash and condensed silica fume together. Thus following conclusions were drawn from an investigation involving the use of a 30% low-calcium fly ash by weight of total cementitious solids together with varying amounts of a silica fume ranging from 5 to 20%, when the W/C ratio of 0.40 was kept constant in all concrete mixtures by the use of a plasticizer.

The 1- and 3-d strengths for concretes incorporating condensed silica fume (Fig. 7) were higher than the control concrete (30% fly ash, 70% portland cement) but lower than concrete containing an equivalent amount of portland cement only. However, due to the intense pozzolanic activity during the 3 to 7-d period, the 7-d strengths of concretes containing 10, 15, or 20% condensed silica fume (in addition to fly ash) were higher than plain portland cement concrete. The strength acceleration advantage associated with the use of silica fume in combination with fly ash is apparent from the fact that the 7-d strengths of concretes incorporating 15 or 20% silica fume were almost twice than that of the strength of concrete with fly ash alone. Furthermore, according to the authors (38), since the strength contribution due to fly ash did not become apparent until after 28 days another important aspect of the combined use of fly ash and condensed silica fume is that, at ages between 7 and 28 days, the loss in compressive strength due to incorporation of 30% fly ash was completely compensated by the addition of as little as 10% condensed silica fume.

A similar approach was successfully taken by Malhotra et al. (39) to enhance the low early-age strength of a portland cement concrete containing pelletized

blast-furnace slag by simultaneously incorporating condensed silica fume. The results of the study are shown in Fig. 8. At a constant $W/(C+BFS)$ ratio of 0.40 and 50% cement replacement level by slag, the strength of the control concrete steadily increased with the increasing additions of silica fume from 5 to 20% level. For instance, at age 7-d, the concrete mixture with 20% silica fume showed almost the same strength as the reference concrete containing no slag. At 28-d, the reference concrete (no slag present) and the control concrete (50% slag present as cement replacement) achieved a similar strength level. However it is noteworthy that during the 7 to 28-d period as little as 5% condensed silica fume was enough to boost the strength of the control concrete to levels that were equal or better than the reference concrete (containing only portland cement).

Mukherjee et al. (40) demonstrated that high strength concretes can be made using more than normal amounts of ordinary (low-calcium) fly ash, provided the cement content of the concrete mixture is high and an adequate dosage of a superplasticizing admixture is used to bring down the $W/(C+FA)$ ratio to < 0.30 . Thus concrete mixtures with about 390 kg/m^3 cement content, 37% fly ash by weight of the total cementitious materials (cement + fly ash), and 0.28 $W/(C+FA)$ ratio, made possible by the use of various superplasticizers, gave at 7, 28, 91, and 365 days compressive strengths on the order of 35-37 MPa, 51-54 MPa, 62-67 MPa, and 63-70 MPa, respectively.

In regard to strength development rates in concrete containing silica fume, when used as a direct replacement (by weight) for portland, Malhotra's (41) data in Fig. 9 shows that there was little or no change in compressive strength at early ages (up to 3-d) for concretes with high water/ $(C+SF)$ ratio of 0.60, regardless of the amount of silica fume used (5 to 15% cement replacement range). However, at the lower $W/(C+SF)$ ratio of 0.4, there was a marked increase in strength at 3-d. The difference is attributed to improvement in the transition zone characteristics, which seems to manifest at an earlier age when condensed silica fume is incorporated in low W/C concretes.

Modulus of elasticity, creep, and drying shrinkage--From the previous review (1) it was concluded that elastic modulus, creep, and drying shrinkage characteristics of concrete are not directly influenced by the incorporation of a mineral admixture into a concrete mixture. Instead, these properties of concrete are largely influenced by the aggregate (both content and stiffness) and by the concrete strength (W/C , curing). Therefore, to the extent the strength development in a concrete is affected by the incorporation of a mineral admixture, its elastic modulus, creep, and drying shrinkage will also be affected. In general, when the strength is reduced, the elastic modulus is also reduced but the creep and drying shrinkage are increased. For instance, compared to plain portland cement concrete, both the compressive strength and elastic modulus for the corresponding concretes containing fly ash (up to 25% cement replacement) are usually lower at early ages but somewhat higher at 90-d and above), and creep and shrinkage are higher at early ages but lower at later ages.

For a variety of reasons, the above guidelines do not work with high-strength concrete. At very low water/cement ratios, (with the use of a superplasticizer), the incorporation of a mineral admixture into concrete causes a considerable improvement in microstructure and strength of the transition zone. As a result, it has been possible to obtain very high levels of compressive strength

in concrete. However, improvements in the transition zone characteristics alone do not appear to be sufficient to cause a corresponding improvement in the elastic modulus of concrete, for which aggregate characteristics become a limiting factor. Even less is known about the influence of the transition zone microstructure on creep and drying shrinkage of concrete. As before, limited data are presented below to illustrate the general principles, which determine the elastic modulus, creep, and drying shrinkage properties of concrete containing by-product mineral admixtures.

From an examination of concretes containing various amounts of fly ashes from different sources, Crow and Dunstan (42) found that both the **modulus of elasticity** and Poisson's ratio increased with age, paralleling the compressive strength development. The modulus of elasticity ranged from a low of 18.8 GPa at 28 days to a high of 39.6 GPa at 365 days. Ghosh and Timusk (43) studied fly ash concretes, proportioned for equivalent 28-d strength, over a range of nominal strength values and concluded that for all strength levels the modulus of elasticity of fly ash concrete was generally similar to the reference concrete. In regard to granulated blast-furnace slag, at 50% cement replacement levels in concrete mixtures, proportioned to have 45 MPa compressive strength at 28-d, Wainwright and Tolloczko (44) found that the 7-d elastic modulus for the slag concrete was 28.5 GPa compared to 36.0 GPa for the reference concrete (without slag), however at 31-d both were in the 38 GPa range, and thereafter only a small increase was observed in the specimens tested at 56-d and 171-d. Similarly, in silica fume concrete mixtures designed for high strength, the elastic modulus values generally do not increase significantly with increasing compressive strength. Malhotra et al's (39) data show that with 47 MPa (28-d) concrete mixtures, both with and without 50% slag replacement, the addition of 5, 10, or 15% silica fume to the slag-cement concretes did not make any difference to the values of the elastic modulus at 28-d, which remained in the 36 GPa range. The highest reported value (43 GPa elastic modulus) in the published literature is for a very low W/C (0.22) concrete, containing 593 kg/m³ cement and 119 kg/m³ silica fume (45). This concrete gave about 100 MPa compressive strength at 28-d.

It is a common experience that fly ash concretes show higher creep strains (compared to control concretes without fly ash) at early ages, and lower creep strains at later ages. ACI Committee 226 (9) concurs that the effects of fly ash on creep of concrete are limited primarily to the extent to which the fly ash influence the strength of concrete. Since high-calcium fly ashes generally do not impact the 28-d strength adversely, data from Yuan and Cook's (46) work showed little difference in creep strains between the control and the test concretes containing 20% fly ash (Fig. 10). It may be noted that with high levels of fly ash incorporation (30 and 50% cement replacement by weight) considerably higher creep strains were obtained. In addition to lower strength, more paste volume (due to the lower density of mineral admixtures compared to portland cement) is responsible for this behavior. For obvious reasons, creep characteristics of concretes containing slag are similar to fly ash concretes. In regard to concrete incorporating silica fume, few published data on creep are available. The 100-MPa concrete mixture when loaded at 28 days with a stress/strength ratio 0.154, showed 330×10^{-6} and 480×10^{-6} creep strains at 3 months and 12 months after loading, respectively (45).

The drying shrinkage behavior of concrete containing mineral admixtures follows generally the creep behavior. Numerous studies have shown that in well-cured concretes the incorporation of up to 25% fly ash did not have any significant effect on the drying shrinkage. Using a low-calcium fly ash, Munday et al. (47) found little difference between the drying shrinkage values of several control concretes (without fly ash) and fly ash concretes (Fig. 11). When the cement replacement level was high, for example, in a slag concrete containing 50% slag by weight of total cementitious solids (48), the drying shrinkage was significantly higher than the control concrete (Fig. 12). Like creep data, the drying shrinkage data for silica fume concretes are scarce. The 100-MPa high strength concrete mixture showed 170×10^{-6} and 315×10^{-6} drying shrinkage values at 3 months and 12 months, respectively (45).

DURABILITY

Expansion and cracking of concrete due to sulfate attack, alkali-aggregate reactions, freezing and thawing, and corrosion of the embedded steel are among the common durability problems, which depend on the permeability of concrete and availability of water. The physical manifestations, mechanisms and control of the chemical causes responsible for lack of concrete durability are discussed in detail elsewhere (33). Water is usually involved in most processes of concrete deterioration; therefore it is the permeability of concrete to water which generally controls the rate of deterioration. Since microcracks in concrete are the principal source of permeability, by reducing the microcracks from a variety of physical and chemical causes the mineral admixtures can have a beneficial effect on general durability of concrete.

Permeability--The quantitative data from water permeability tests on concrete are generally not reliable because of experimental problems, such as the difficulty to achieve a steady state of flow. However, Berry and Malhotra (49) cited studies dated as far back as 1950's to show that well-cured (age 6 months) concrete pipe containing 30 or 50% fly ash as cement replacement were approximately five times as impermeable as the corresponding concrete without the fly ash. The authors also cited recent data from water permeability tests on cement pastes by Manmohan and Mehta, and chloride ion permeability tests by Short and Page, which confirm earlier work.

Douglas (50) cited Kondo et al. as well as Bakker's work on cement mortars to show that, with curing age, the diffusion coefficient in slag cement mortars diminished faster than the diffusion coefficient in a portland cement mortar, and that slag cement mortars were 10 to 100 times less permeable to water than portland cement mortar. Bakker (51) has given extensive data on diffusion coefficients of Na^+ , K^+ , and Cl^- ions in 0.50 to 0.65 W/C mortars made with blended portland cements, containing 60 or 75% slag.

As condensed silica fume is highly pozzolanic compared to fly ash or slag, it decreases the concrete permeability rapidly. Results from studies by Markestad (52) and Gjorv (53) on water permeability of concretes in which the cement content varied from 100 to 500 kg/m^3 showed that a lean concrete mixture incorporating 100 kg/m^3 cement and only 10% condensed silica fume had its

20 Mehta

permeability decreased to about 4×10^{-10} m/sec, compared to 1.6×10^{-7} m/sec without the silica fume. The permeability of concrete containing 100 kg/m³ cement and 20% silica fume was similar to the one containing 250 kg/m³ cement and no silica fume. At high cement contents, the degree of effectiveness of silica fume in reducing the permeability of concrete was diminished.

Sulfate attack--When used as cement replacement, there is a general belief that most low-calcium fly ashes would improve the resistance of concrete to sulfate water, however most high-calcium fly ashes would reduce it. From an experimental study, Dunstan (54) developed an empirical sulfate resistance factor (R), calculated as follows: $R = (C-5)/F$, where C is % CaO and F is % Fe₂O₃ in fly ash. At 25% cement replacement level, Dunstan found that when R is less than 1.5, the sulfate resistance of the fly ash concrete was improved; however, when R is higher than 3.0 the sulfate resistance was reduced. Mehta (55) cited the work of several researchers including his own to conclude that Dunstan's R-factor does not provide a reliable method for predicting the suitability of fly ashes for use in sulfate-resisting concretes. From microstructural examination of blended cement pastes containing a variety of fly ashes, the author found that a more rational correlation than given by Dunstan existed between sulfate resistance of concrete and mineralogical composition of the products formed as a result of fly ash-portland cement interaction. Irrespective of the calcium content or the R-factor, it is the amount of reactive alumina contributed by a fly ash (from the dissolution of the aluminosilicate glass and hydration of crystalline compounds, such as C₃A and C₄A₃S̄), which controlled the presence of the minerals highly vulnerable to sulfate attack (such as the monosulfate hydrate and calcium aluminate hydrates).

From a laboratory investigation involving the evaluation of sulfate-resisting behavior of blended portland cements containing 25 or 40 wt. % of fly ashes with widely varying R-factors, the author (55) found that some lignitic and subbituminous fly ashes, with high calcium and sulfate contents (high R-factor), as a result of fly ash-cement interaction, formed ettringite as a stable product of hydration before exposure to the sulfate solution. Therefore well-cured cement pastes containing these fly ashes did not show the characteristic expansion and strength loss on sulfate exposure. On the contrary, some low-calcium bituminous fly ashes, with low R-factor but high contents of reactive alumina in glass, formed the monosulfate hydrate as a result of fly ash-cement interaction and, therefore the corresponding cement pastes containing these fly ashes showed considerable strength loss on sulfate exposure.

As with fly ash, when the use of ground slag leads to a reduction in concrete permeability and calcium hydroxide content, these effects would enhance the sulfate-resisting characteristic. Studies have shown that, at low cement replacement levels, alumina content of glass in slag would also influence the sulfate resistance adversely. Recent work reported by Frearson (56) confirmed the inferior resistance to sulfate attack of blended portland cements containing low levels of granulated slag replacement.

However, many studies have confirmed that the combinations of portland cement and ground granulated blast-furnace slag, in which the slag content is greater than 60%, are generally sulfate-resisting, irrespective of the C₃A content of the portland cement and the alumina content of the slag. According to Bakker (51), this is due to very low permeability of the concrete to ionic diffusion.

Douglas (50) cites two recent studies on sulfate resistance of blended cements composed of 50% ASTM Type I portland cement (12% C_3A) and 50% Canadian pelletized slag (7% Al_2O_3). Both laboratory and field tests have shown that concretes made with these cements were as resistant to sulfate attack as the corresponding concretes made with sulfate-resisting portland cements (ASTM Type V).

Condensed silica fume, even in relatively small amounts (10 to 15% wt. cement replacement), is quite effective in reducing the microporosity and permeability of concrete, in addition to causing a lowering of the calcium hydroxide content and the C/S ratio of the CSH in the hydrated cement paste. As a result, concretes incorporating silica fume can be impermeable and highly resistance to aggressive chemical solutions such as sodium or magnesium sulfates, and even dilute acids. An investigation on the relative chemical resistance of low W/C (0.33) concretes containing silica fume showed that when exposed for 6 months to 1% HCl, 1% lactic acid, and 5% acetic acid solutions, the silica fume concretes generally exhibited better performance than either the reference concrete (without any admixture) or a latex-modified concrete (57).

Alkali-aggregate expansion--Recent reports on the effectiveness of fly ash and slag in reducing the alkali-aggregate expansion are consistent with the conclusions of the previous review (1). There is sufficient evidence to show that low-calcium fly ash are effective in reducing expansion caused by alkali-silica reactions in concrete when used at a replacement level in the range of 25 to 30% or more. With high-calcium fly ash higher replacement levels may be needed to reduce the expansion. When a high-calcium fly ash contains large amounts of alkali sulfates, it tends to increase the amount of water-soluble alkalies in concrete. It is generally believed that deleterious alkali-aggregate activity occurs only when the total amount of water-soluble alkalies in concrete from all sources exceed 2.5 kg/m^3 .

Using Beltan Opal as a reactive aggregate, Hobb (58) concluded that reduction of alkali-silica expansion by fly ash or slag incorporation is mainly due to the "alkali dilution" effect and, also that slags were generally more effective in reducing the deleterious expansion than fly ash. However, using other reactive aggregates, both Nixon and Gaze (59), and Oberholster and Westra (60) found that fly ash was generally more effective than slag, and that the reduction in expansion was found to be greater than expected from simple dilution effect on the alkali content of concrete. This is possibly due to the added effect of low permeability to ionic diffusion in systems containing fly ash or slag. Also, recent work by Sersale and Frigione (61) confirmed that about 50% cement replacement by a blast-furnace slag was required, compared to about 30% cement replacement by a low-calcium fly ash, to reduce the expansion in mortar bars made with a high-alkali portland cement to $< 0.1\%$ level.

Similar to rice husk ash (1), relatively small amount of condensed silica fume should be effective in reducing the deleterious alkali-aggregate expansion, however little published data are available. Malhotra et al. (6) cite a field test reported by Aitcin on a concrete pavement in Quebec, which was built in 1980. The concrete contains an alkali-reactive aggregate (limestone containing amorphous silica) which is known to cause deleterious expansion in structures within 1 year. The cement content of concrete in various parts of the pavement

22 Mehta

ranged from 140 to 405 kg/m³, and replacement of cement by condensed silica fume ranged from 10 to 40 wt. %. At the time of the last inspection, three years after the construction, the pavement was in good condition with no deleterious expansions, although traces of alkali-silica gel were found in the cores from the high cement content concrete.*

Corrosion of steel in concrete--The reinforcing steel in concrete remains covered with a passive iron oxide film, which must be destroyed before the electrochemical reactions resulting in steel corrosion can begin. The depassivation of steel can occur in the presence of chlorides or when the pH of concrete is reduced to < 11 by acid attack, such as by carbonation. Once the steel has been depassivated, the progress of corrosion would be controlled by the rates of oxygen and moisture flow to the steel and the electrical resistivity of concrete.

Through incorporation of mineral admixtures, by influencing the various factors involved in steel corrosion as mentioned above, it should therefore be possible to exercise considerable effect on the expansion and cracking of concrete from the corrosion of steel. In order of decreasing importance, the key factors controlling the degree of corrosion of steel in a concrete appear to be permeability, resistivity, and carbonation. The permeability of concrete is most important not only because it controls the rates of carbonation or chloride ingress essential for initiating the corrosion process, but also the rates of oxygen and moisture flow which would influence the progress of the corrosion process. A review of the beneficial effect of mineral admixtures on microporosity and in permeability of cement paste was presented in the previous report (1). The author believes now that in concrete the incorporation of mineral admixture can lead to even better results by strengthening the transition zone, because microcracks in the transition zone are the major source of concrete permeability.

Due to the lower amounts of calcium hydroxide available in concretes containing mineral admixtures, there has been a concern about their carbonation behavior. From a review of several publications, Berry and Malhotra (49) concluded that well-compacted and properly cured concretes, with low W/C ratio, appear to be sufficiently impermeable to resist the advance of atmospheric carbonation beyond the first few millimeters. The authors cited a study by Ho and Lewis, in which an inverse relationship was found between the concrete strength and depth of carbonation, e.g. at strength levels lower than 30 MPa the fly ash concrete was more readily carbonated than the reference concrete without fly ash. This happened when the concretes were exposed to carbonation at a given age, rather than at an equivalent strength. The fly ash concretes cured to 90 days before carbonation, showed a lower rate of carbonation compared to the reference concrete. In conclusion, compared to normal concrete, a fly ash concrete would not decrease the corrosion protection of reinforcing steel provided it contained good-quality fly ash, proper mix proportions, and has received adequate curing prior to environmental exposure.

*Recent core tests by the author, seven years after the construction of the pavement, also indicate no deleterious expansions due to the alkali-aggregate reactivity (personal communication from Professor P.C. Aitcin, June, 1988).

In concrete made with a cement containing a relatively large amount of slag (50 to 75 wt. %), greater carbonation depths compared to control concrete have been reported by some researchers. For instance, Litvan and Meyer (62) found that the long-term depths of carbonation were greater in a slag concrete. This was attributed to the coarsening of the pore size distribution as a consequence of carbonation of the slag-cement paste. On the contrary, due probably to calcium carbonate formation by chemical reaction between Ca(OH)_2 and CO_2 and subsequent sealing of large pores, the reference concrete containing portland cement showed a decreasing carbonation rate with age. Evidently, as Berry and Malhotra (49) concluded, the solution lies in using a low W/C ratio, high cement content, and adequate consolidation and curing of concrete so that carbonation can be stopped at the concrete surface.

In regard to silica fume concretes, Vennesland and Gjorv (63) and Gjorv (53) reported the results of 10 or 20% silica fume incorporation on the rate of oxygen transport, carbonation, and electrical resistivity. Although, as a result of silica fume incorporation, the rate of oxygen transport through water-saturated concrete as well as the depth of carbonation were only slightly reduced in ordinary concrete mixtures [low cement contents and high $W/(C+SF)$ rates], the electrical resistivity was significantly enhanced. In a high-strength concrete mixture with 400 kg/m^3 cement content, 20% silica fume, and 0.38 $W/(C+SF)$, the electrical resistivity was enhanced from about 9 to about 127 K ohm/cm as a consequence of silica fume addition. This, obviously, would have a dramatic effect on reducing the corrosion potential of steel in concrete containing condensed silica fume.

Thermal strain--Not only in concrete dams but also in large foundations, piers, columns, and beams, the heat of hydration of cement can be of such magnitude as to require special attention to prevent excessive temperature rise, which is followed by shrinkages and cracking when the structure cools down to ambient temperature. Serious cracks jeopardize the structural safety and, more importantly, increase the permeability of concrete which exposes the structure to other processes of deterioration. Depending on the size and shape of a structure, cement type and content, and concrete temperature at placement, adiabatic temperature rise of the order of 30 to 50°C is not uncommon in massive structures made with ordinary concrete. Even higher temperatures may be experienced with high-strength concrete mixtures. In the case of plain portland cement concretes, the peak temperature may be reached within 2 to 5 days after placement and the structure will develop thermal cracking if the rate of cooling to ambient temperature is high.

As described in the previous report (1), one of the ways to reduce the rate of temperature rise significantly is to replace a part of the cement by a mineral admixture. Thus the use of mineral admixtures, such as fly ash, provides an effective means of controlling thermal shrinkage cracking in concrete without compromising the ultimate desired strength.

In the United States most concrete gravity dams built during the last 30 years contain 25 to 35% fly ash by weight of cement, and a similar proportion of fly ash is used in several recently constructed roller-compacted concrete dams. At 30% cement replacement levels by fly ash, the reduction in temperature rise of concrete is about 15%. Other advantages associated with the use of fly ash in mass concrete are its water-reducing ability (therefore the possibility of further cement reduction

24 Mehta

at a given W/C), and the thermal activation potential, which is superior to portland cement. At high curing temperatures, not only the rate of hydration of even a coarse-grained fly ash becomes high, but also the microstructure and mechanical properties of the portland cement-fly ash paste are usually superior to the neat portland cement pastes (42).

Like fly ash, the incorporation of ground slag as a partial substitute for cement reduces the early rate of heat generation, and this reduction is directly proportional to the proportion of slag used. Depending on their reactivity, the adiabatic temperature rise may be slightly lower with portland-slag cements than portland-fly ash cements because the former usually contain 50 to 70% of the blending component compared to 20 to 30% for the latter. In mass concrete, from in situ measurements of relative temperature rise of concrete mixtures (400 kg/m³ cementitious solids) containing a portland-slag cement (75% slag), a portland-fly ash cement (30% fly ash), and a neat portland cement, Bamforth (64) found that the concrete showed 46°C, 47.5°C, and 54.5°C temperature rise, respectively, thus confirming that the effect of cement replacement by each of the mineral admixtures was to reduce the peak temperature by about 15%.

There is little published data regarding the effect of **condensed silica fume** incorporation on temperature rise in concrete. With a 100 MPa superplasticized concrete mixture containing 500 kg/m³ silica fume, Aitcin et al. (65) reported that the first increase in the temperature of concrete was recorded only after 17.5 hours of placement. There is another reported case where a part of the cement was replaced by silica fume in order to reduce the risk of thermal cracking in a high-strength concrete (33). In the slip-formed pylons of the new Tjorn Bridge in Sweden, 370 kg/m³ of cement and 37 kg/m³ of silica fume were used for making a 62 MPa concrete (28-d). Additionally, artificial cooling of the structure by circulation of cold air helped to lower the peak concrete temperature by 10 to 12°C.

In the previous review (1), a laboratory investigation was reported on the adiabatic temperature rise in high-strength (6000 psi) concrete, containing a rice husk ash-portland cement (30% ash). Compared to the reference concrete, the rice husk ash concrete developed higher strengths but less temperature rise at 7 and 28-d. For application to high-strength concrete this is important information that certain pozzolan-cement combinations are capable of producing higher strength per unit of temperature rise than portland cement alone, even at early ages.

Frost action--When portland cement concrete is to be exposed to cycles of freezing and thawing, it must be protected from expansion and cracking by the use of air entrainment. Air content, bubble spacing, and specific surface are the most important parameters for evaluating the effectiveness of air entrainment. For satisfactory resistance to freezing and thawing, the generally accepted values are between 4 and 7% for entrained air content, < 200 μ m for the bubble spacing factor, and > 24/mm specific surface.

As with all portland cement concrete, in freezing and thawing environments proper air entrainment is necessary for protection of concretes containing mineral admixtures. From a study of relative frost resistance of concretes, both with and without mineral admixtures, Virtanen (66) found that **non-air-entrained** concretes incorporating slag, fly ash, or condensed silica fume showed poorer results than

the reference portland cement concretes. However, air-entrained concretes containing slag, fly ash, or silica fume showed better resistance than the corresponding portland cement concretes.

ACI Committee 226 (9) cautions that care should be exercised in proportioning mixtures to insure that not only concretes have adequate strength (3500 psi or more) when first exposed to freezing and thawing cycles but they should also be at a comparable level of maturity. For example, because of the slower strength gain in concrete with low-calcium fly ash at normal ambient temperatures, more cementitious material (cement + fly ash) is generally used to achieve comparable maturity at 28 days. This increased amount of cementitious material often requires an increase in the amount of air-entraining admixture per unit volume of concrete in order to obtain equivalent air contents.

Larger than normal dosages of air-entraining admixtures are also needed in the case of low-calcium fly ashes which contain relatively high proportion of carbon (due to high adsorption of air-entraining admixture by the carbonaceous particles with large specific surface). In the event of application of deicers, due probably to their finer pore structures the concretes containing mineral admixtures, even when air-entrained, are generally more vulnerable to surface scaling (higher loss of surface mortar) than the corresponding portland cement concretes. Similarly, as the quantity of fly ash in air-entrained concrete is increased to very high proportions, more scaling damage is likely to occur. The preceding conclusions are confirmed by several studies cited by Berry and Malhotra (49).

Douglas (50) cited several recent investigations on frost action of concrete containing granulated blast-furnace slag as a partial replacement for cement. With proper air entrainment equivalent or even better performance is reported with slag cement, when compared to portland cement. Denser and more uniform microstructure and finer pore system in the hydrated cement paste containing slag is credited for their superior performance provided the strengths and air contents are kept constant before subjecting the specimens to freezing and thawing tests.

Regarding the frost resistance of silica fume concrete, conflicting results have been reported in the literature. Probably differences in test methods, when dealing with cement paste systems containing very fine pores, are responsible for this. Because of sluggish water movement the response of such microporous systems to freezing and thawing cycles depends on the degree of saturation. Earlier reports raised the possibility that, due to lack of freezable water in very low W/C superplasticized cement pastes containing silica fume, even non-air-entrained concrete would perform well under freezing and thawing environments. When ASTM Method C 666 (Procedure A or B) is used, Malhotra et. al (6) conclude that non-air-entrained concrete, regardless of the W/(C+SF) ratio, and irrespective of the amount of condensed silica fume, shows very low durability factors and excessive expansion. The concrete appear to show increasing distress with increasing amounts of the silica fume. On the other hand, air-entrained concrete, regardless of the W/(C+F) ratio and containing up to 15% condensed silica fume as partial replacement for cement, performs satisfactorily. However, concrete containing 20 and 30% silica fume, and with W/(C+SF) ratios of the order of 0.4, tends to perform poorly.

Surface wear by abrasion-erosion--Resistance of concrete to abrasion-erosion is greatly influenced by the strength characteristic of the aggregate. With a given aggregate type, the strengths of the cement paste and the transition zone govern the rate of surface wear. Since both depend on the water/cement ratio and the curing conditions, it should be obvious that the influence of a blended portland cement on the abrasion-erosion resistance of concrete would be determined by the degree to which it modifies the water/cement ratio and the curing requirements of the reference portland cement.

There is little published information on the abrasion-erosion resistance of concretes containing fly ash, slag, and condensed silica fume. In part, this is due to cumbersome and unsatisfactory standard test methods. Berry and Malhotra (49) cite a study by Liu who, using an underwater abrasion test, compared the rates of surface wear between a reference concrete and a corresponding fly ash concrete (25% fly ash by volume replacement for portland cement). Both the concretes had similar strengths (about 50 MPa) before testing. This was achieved by curing the fly ash concrete for 90 days compared to 28 days for the reference concrete. Little difference in abrasion resistance was found between the two concretes for test periods up to 36 hours, however after 72 hours the fly ash concrete showed 7.6% weight loss compared to 6.1% for the reference concrete. Berry and Malhotra (49) concluded that more research is urgently needed to evaluate the abrasion-erosion of fly ash concrete under many forms of exposure.

Gjorv et al. (67) reported from a recent study that a very high-strength concrete mixture (150 MPa) containing a quartz-diorite aggregate, condensed silica fume, and a superplasticizer, showed an abrasion or wet-erosion loss of the same order as that of a granite element used for reference purpose. Since under severe abrasion-erosion conditions the failure of the cement paste-aggregate bond results in aggregate pull-out, by strengthening the transition zone with the help of condensed silica fume and a very low W/C ratio it seems possible to enhance greatly the abrasion-erosion resistance of concrete surfaces.

STANDARD SPECIFICATIONS AND TEST METHODS

Several recent reports (68-71) deal with the important issue of standard specifications and test methods for pozzolanic and cementitious admixtures for concrete. There has been a general dissatisfaction with the current world standards on fly ash and slag (and only Norway and Canada have standard specifications covering silica fume). The principal reason for this dissatisfaction is that there are too many mandatory physical and chemical requirements, which do not seem to serve the interests of either producers or consumers of mineral admixtures.

From a critical examination of the significance of various physical and chemical requirements in the present standards (10, 68), it is concluded that a few carefully selected requirements should be able to serve the twin purposes of insuring uniformity, in quality, and a desired level of performance by the material when incorporated in concrete. Irrespective of the type or source of a siliceous by-product, it appears that only ignition loss, fineness, and activity index with portland cement are the material characteristics that justify mandatory testing

and control. Such a simplified approach can eventually lead to a global standard covering all mineral admixtures (68).

Recent trends, e.g., the development of a new Canadian Standard (CAN/CSA-A23.5-M86) covering all mineral admixtures including silica fume, seem to justify the move away from materials specific to performance-specific standards. In the closure to a discussion on the final report of RILEM Technical Committee on Siliceous By-products in Concrete (10), the Committee stated, "We would like to reiterate that **the materials-specific standards for mineral admixtures have outlived their usefulness.** To serve equally the interests of both producers and users of pozzolanic and cementitious by-products, we believe that a global standard is needed. When accompanied by proper explanations containing a summary of factors that influence the durability of concrete containing siliceous additions, a global standard can be made to serve another important purpose, namely the general consumer education in concrete durability."

ECOLOGICAL BENEFITS

The previous report (1) contains a brief reference to economic, energy-conserving, and ecological benefits that are possible from the incorporation of cementitious and pozzolanic by-products in concrete. Recently, Kreijger (72) presented an interesting approach to compare the ecological profile of various materials of construction. The ecological profile takes into consideration various parameters, such as desoiling and deforestation for the recovery of raw materials, and pollution caused from dust and SO₂ emissions. From comparison of their ecological profiles, the authors concluded that reinforced concrete is the most environmental-friendly material for construction work.

Since unused industrial by-products cause land, air, and water pollution, the environmental-friendliness of concrete can be greatly enhanced by incorporating pozzolanic and cementitious by-products in most of the concrete being produced today. The economic and engineering benefits, such as durability enhancement of using mineral admixtures in concrete are already well established. Therefore, when the environmental benefits of using concrete containing fly ash, slag, and silica fume are also considered, the product acquires a highly attractive position among all building materials. It is for the construction industry to make a better use of this knowledge and to increase the rates of utilization of pozzolanic and cementitious by-products in concrete than is the case today (see Table 1). There is already a growing consciousness in society that builders of projects must be held accountable for social and ecological consequences of their actions, including the selection of environmental-friendly materials for construction.

A RECENT DEVELOPMENT

The practice of using large proportions of fly ash in mass concrete mixtures is well known. Besides cost economy and reduction of heat of hydration, the incorporation of fly ash into lean concrete mixtures generally helps to improve the workability because most fly ashes have a plasticizing or water-reducing effect in

concrete. For instance, in a recent investigation with a non-air-entrained lean concrete mixture containing 210 kg/cm^3 water, Ravina and Mehta (73, 74) substituted 35 to 60% cement by mass with fly ash and reduced the water content by as much as 18% while maintaining a constant consistency (55 mm slump). With a typical ASTM Class F fly ash ($350 \text{ m}^2/\text{kg}$ Blaine, 18% residue on No. 325 mesh, 3.5% ignition loss) although the early strengths up to 28-d were less than the control, the 90-d strengths were comparable and the 1-yr strengths were higher by approximately 50%. It should be noted that, when compared to the control concrete, with high fly ash concrete the improvement in ultimate strength resulted both from a decrease in the $W/(C+F)$ ratio and an increase in the total cementitious materials.

Malhotra and his colleagues (75, 76) have made an important contribution to the state of the art by investigating the properties of high-workability concrete mixtures, with $W/(C+F)$ ratio reduced to as low as 0.3 by the simultaneous use of a large amount of fly ash and chemical admixtures, such as superplasticizing and air-entraining agents. For example, using 150 kg/m^3 of an ASTM Type II portland cement, 190 kg/m^3 of a Class F fly ash [$F/(C+F) = 0.56$], a water content corresponding to $W/(C+F)$ ratio of 0.33, a naphthalene sulfonate type superplasticizer, and an air entraining agent, Malhotra (75) made concrete mixtures having 40 to 110 mm slump and 4 to 6% air content. The 28-d compressive strengths ranged from 28–35 MPa, and the average compressive strength at 3-months was approximately 40 MPa. A subsequent report (76) showed that a superplasticized concrete mixture with the same $F/(C+F)$ ratio of 0.56, but a lower cement content (100 kg/m^3) and a higher $W/(C+F)$ ratio 0.49 (which, incidently, is similar to one of the unsuperplasticized mixtures of Reference No. 73 and 74), gave 23 and 38 MPa compressive strength at age 28-d, and 91-d, respectively.

For comparison purposes, data on the influence of high volume of fly ash on strength characteristics of lean concrete mixtures, both with and without the presence of superplasticizing and air entraining admixtures, are shown in Table 4. In spite of 4% entrained air in the superplasticized concrete mixture containing 100 kg/m^3 cement, the concrete showed considerably greater strengths at 28 and 90-d than the unsuperplasticized mixture containing a higher cement content (120 kg/m^3). This may be attributed to a better dispersion of cement and fly ash particles and a more uniform microstructure of the hydration products in the superplasticized concrete. Although the same materials were not used by the investigators (74, 76), minor differences in the physical-chemical characteristics of fly ash and portland cement are not expected to influence the strength results at 28, 90, and 365-d.

In addition to compressive strength, Langley et. al (76) also investigated other properties of low cement content, high fly ash content, superplasticized, air-entrained concrete mixtures. The authors concluded that the test mixtures compared well with control concrete mixtures containing no fly ash with regard to elastic properties, drying shrinkage, creep, and resistance to freezing and thawing cycles.

CONCLUDING REMARKS

The use of pozzolanic and cementitious by-products or mineral admixtures in portland cement concrete is generally beneficial from standpoint of cost economy and enhancement of properties of both fresh and hardened concrete. The degree to which a particular property is improved and the rate at which an improvement occurs do not depend on the type or the source of the mineral admixture. There is increasing scientific evidence that they depend on the mineralogical and granulometric characteristics of the admixture used.

It is not difficult to understand why, for a given mix proportion, the rheological behavior of a fresh concrete mixture would be influenced more by the particle shape and size distribution (fineness) of the mineral admixture than by its type (i.e., whether it is fly ash or slag). However, only recently there is an increasing appreciation of the fact that the engineering properties of hardened concrete are also controlled by the particle characteristics and mineralogy and not by the type of the mineral additive. This is because the granulometry and mineralogy of the reactants influence the reaction rates, which determine the microstructure of the cement-mineral admixture interaction products and hence the engineering properties. Thus, from standpoint of the effect of a mineral admixture on the properties of concrete, it is less important whether the admixture is a fly ash or a slag, but more important how fine is the particle size, and whether the noncrystalline and the crystalline phases present are more active or less active to hydration.

REFERENCES

1. Mehta, P. K., "Pozzolanic and Cementitious By-products as Mineral Admixtures for Concrete - A Critical Review," ACI SP-79, 1983, pp. 1-46.
2. Berry E. E., and Malhotra, V. M., Fly Ash in Concrete, CANMET Publ. SP 85-3, Ottawa, Canada, 1986, 178 pages.
3. Swamy, R. N. (editor), Cement Replacement Materials, Surrey Univ. Press, 1986, 259 pages.
4. Helmuth, R. A., Fly Ash in Cement and Concrete, Portland Cement Assoc., 1987, 203 pages.
5. Malhotra, V. M. (editor), Supplementary Cementing Materials for Concrete, CANMET Publ. SP 86-8E, 1987, 428 pages.
6. Malhotra, V. M., Ramachandran, V. S., Feldman, R. F., and Aitcin, P. C., Condensed Silica Fume in Concrete, CRC Press, 1987, 221 pages.
7. ACI Committee 226, "Silica Fume in Concrete", ACI Materials Jour., March-April, 1987, pp. 158-166.

30 Mehta

8. ACI Committee 226, "Ground Granulated Blast-Furnace Slag as a Cementitious Constituent in Concrete", ACI Materials Jour., July-Aug., 1987, pp. 327-342.
9. ACI Committee 226, "Fly Ash in Concrete", ACI Materials Jour., Sept.-Oct., 1987, pp. 381-409.
10. RILEM 73-SBC Committee, "Siliceous By-products for Use in Concrete", Materials and Structures, Jan. 1988, pp. 69-80.
11. Mehta, P. K., "Testing and Correlation of Fly Ash Properties with Respect to Pozzolan Behavior", EPRI Report CS 3314, Jan. 1984.
12. Aitcin, P. C., Pinsonneault, P., and Roy, D. M., "Physical and Chemical Characterization of Condensed Silica Fume", Am. Ceram. Soc. Bull., 63, 1984, p. 1487.
13. Helmuth, R. A., "Water-reducing Properties of Fly Ash in Cement Pastes, Mortars, and Concretes: Causes and Test Methods", ACI SP-91, 1986, pp. 723-740.
14. Hemmings, R. T., and Berry, E. E., "The Role of Non-crystalline Phases in the Activation of Metallurgical Slags", Proc. Int'l Workshop on Granulated Blast-Furnace Slag in Concrete, Toronto, Canada, 1987, pp. 441-458.
15. Diamond, S., and Lopez-Flores, F., "On the Distribution Between Physical and Chemical Characteristics Between Lignitic and Bituminous Fly Ashes", Proc. Symp. on Effects of Fly Ash Incorporation in Cement and Concrete, Materials Research Soc., 1981, pp. 34-44.
16. Diamond, S., "On the Glass Present in Low-Calcium and High-Calcium Fly Ashes", Cem. Concr. Res., Vol. 13, 1983, pp. 459-464.
17. Roode, M., and Hemmings, R. T., "Development of a Unified Theory for Predicting the Behavior of Glassy Waste Products", CANMET Contract Report, No. ISQ83-00162, July 1985.
18. Hemmings, R. T., and Berry, E. E., "On the Glass in Coal Fly Ashes: Recent Advances", Proc. Mat. Res. Soc. Symp., No. 113, 1988.
19. McCarthy, G. J., Swanson, K. D., Keller, L. P., and Blatter, W. C., "Mineralogy of Western Fly Ashes", Cem. Concr. Res., Vol. 14, 1984, p. 471-478.
20. Mehta, P. K., "Influence of Fly Ash Characteristics on the Strength of Portland Cement-Fly Ash Mixtures", *ibid.*, Vol. 15, 1985, pp. 53-64.
21. Idorn, G., and Henrikson, "State of the Art for Fly Ash Uses in Concrete", *ibid.*, Vol. 14, No. 4, 1984, pp. 463-470.
22. Hooton, R. D., "The Reactivity and Hydration Products of Blast-furnace Slag", Chapter 4 of Reference No. 5, 1987, pp. 247-288.

23. Demoulian, E., Gourdin, P., Hawthorn, F., and Vernet, C., "Influence of Slag Chemical Composition and Texture on their Hydraulicity", Proc. 7th Int'l. Congress on the Chemistry of Cements, Paris, Vol. 2, 1980, pp. III 89-94.
24. Frearson, J. P. H., and Uren, J. M., "Investigation of a Ground Granulated Slag Containing Merwinitic Crystallites", ACI SP-91, 1986, pp. 1401-1421.
25. Harrison, A. M., Winter, N. B., and Taylor, H. F. W., "Microstructure and Microchemistry of Slag Cement Pastes", Proc. Mat. Research Soc. Symp., No. 86, 1987, pp. 199-208.
26. Mehta, P. K., "Testing and Correlation of Fly Ash Properties with Respect to Pozzolanic Behavior", Elec. Power Research Inst., Report No. CS-3314, 1984.
27. Cheng-yi, H., and Feldman, R. F., "Influence of Silica Fume on the Microstructure Development in Cement Mortars", Cem. Concr. Res., Vol. 15, 1985, pp.285-291.
28. Mehta, P. K., and Gjorv, O. E., "Properties of Portland Cement Concrete Containing Fly Ash and Condensed Silica Fume", Ibid., Vol. 12, 1982, pp. 587-593.
29. Sellevold, E., and Nilson, T., "Condensed Silica Fume in Concrete - A World Review", Chapter 3 of Reference No. 5, 1987, pp. 167-243. 30. Feldman, R. F., "Pore Structure Damage in Blended Cements Caused by Mercury Intrusion", J. Am. Ceram. Soc., Vol. 62, No. 1, 1984, p. 30.
30. Feldman, R. F., "Pore Structure Damage in Blended Cements Caused by Mercury Intrusion", J. Amer. Ceram. Soc., Vol. 62, No. 1, 1984, p. 30.
31. Kaizaki, K., Mino, I., and Sakai, E., "Microstructure and Phase Composition of Hardened Ultra High Strength Cement", Rev. 41st Gen. Meeting, Cem. Assoc. of Japan, 1987, pp. 48-51.
32. Andersson, R., and Gram, H., "Properties of Alkali Activated Slag Cement", Nordic Concrete Res., Publ. No. 6, 1987, pp. 7-18.
33. Mehta, P. K., Concrete: Structure, Properties, and Materials, Prentice-Hall, Inc., 1986, 450 pages.
34. Mehta, P. K., "Mechanisms by Which Condensed Silica Fume Improves Concrete Strength", Proc. Workshop on Condensed Silica Fume in Concrete, Montreal, 1987, pp.
35. Monteiro, P. J. M., and Mehta, P. K., "Improvement of the Aggregate-Cement Paste Transition Zone by Grain Refinement of Hydration Products", Proc. 8th Int'l Congress on the Chemisty of Cements, Rio de Janeiro, Vol. 3, 1986, pp. 433- 437.

32 Mehta

36. Detwiler, R., Krishnan, K., and Mehta P. K., "Effect of Granulated Blast-Furnace Slag on the Transition Zone in Concrete", ACI SP-100, Vol. 1, 1987, pp. 63-72.
37. Mehta, P. K., "Hardened Cement Paste - Microstructure and its Relationship to Properties", Proc. 8th Int'l Congress on the Chemistry of Cements, Rio de Janeiro, Vol. 1, 1986, pp. 113-121.
38. Carette, G. G., and Malhotra, V. M., "Early-age Strength Development of Concretes Incorporating Fly Ash and Silica Fume", ACI SP-79, 1983, pp. 765-784.
39. Malhotra, V. M., Carette, G. G., and Aitcin, P. C., "Mechanical Properties of Portland Cement Concrete Incorporating Blast-furnace Slag and Condensed Silica Fume", Proc. Int'l. Symp. on Concr., Monterey, Mexico, 1985, pp. 395-414.
40. Mukherjee, P. K., Loughborough, M. T., and Malhotra, V. M., "Development of High-strength Concrete Incorporating a Large Percentage of Fly Ash and Superplasticizers", ASTM J. Cem. Concr. and Aggr., Vol. 4, 1983, pp. 81-86.
41. Malhotra, V. M., "Mechanical Properties and Freezing and Thawing Resistance of Non Air-Entrained and Air-Entrained Condensed Silica Fume Concretes Using ASTM Test C 666 Procedures A and B", CANMET Report MRP/MSL 84-153, 1984.
42. Crow, R. D., and Dunstan, E. R., "Properties of Fly Ash Concrete", Proc. Mat. Res. Soc. Symp. on Fly Ash Incorporation, Boston, 1981, pp. 214-225.
43. Ghosh, R. S., and Timusk, J., "Creep of Fly Ash Concrete", ACI Jour., Vol. 78, No. 5, 1981, pp. 351-357.
44. Wainwright, P. I., and Tolloczko, J. J. A., "Early and Later Age Properties of Temperature Cycled Slag-OPC Concretes", ACI SP-91, 1986, pp. 1293-1322.
45. Wolsiefer, J., "Ultra High-Strength Field Placeable Concrete with Silica Fume Admixture", ACI Concr. Int'l., Vol. 6, No. 4, 1984, p. 25.
46. Yuan, R. L., and Cook, J. E., "Study of a Class C Fly Ash Concrete", ACI SP-79, 1983, pp. 307-319.
47. Munday, J. G. L., Ong, L. T., Wong, L. B., and Dhir, R. K., "Load Independent Movements in OPC/PFA Concrete", Proc. Int'l Symp. on the Use of PFA in Concrete, University of Leeds, 1982, pp. 243-261.
48. Hogan, F. J., and Mensel, J. W., "The Evaluation for Durability and Strength Development of Ground Granulated Blast-furnace Slag", ASTM, J., Cem., Concr., and Aggr., Vol. 3, No. 1, 1981, pp. 40-52.

49. Berry, E. E., and Malhotra, V. M., "Fly Ash in Concrete", Chapter 2 of Reference No. 5, 1987, pp. 37-163.
50. Douglas, E., "Blast-furnace Slag Cement Mortar and Concrete: Durability Aspects", *ibid.*, Chapter 6 of Reference No. 5, 1987, pp. 337-369.
51. Bakker, R. F. M., "La Durabilite des Betons de Ciment de Haut Fourneau", *Silicates Industriels*, 1982-3, pp. 91-95.
52. Markestad, A., "An Investigation of Concrete in Regard to Permeability Problems and Factors Influencing the Results of Permeability Tests", *Sintef Res. Report 65A 77077*, NTH Trondheim, Norway, 1977.
53. Gjorv, O. E., "Durability of Concrete Containing Condensed Silica Fume", *ACI SP-79*, 1983, p. 695.
54. Dunstan, E. R., "A Possible Method for Identifying Fly Ashes That Will Improve the Sulfate Resistance of Concretes", *ASTM, J. Cem. Concr. and Aggr.*, Vol. 2, No. 1, 1980, pp. 20-30.
55. Mehta, P. K., "Effect of Fly Ash Composition on Sulfate Resistance of Cement", *ACI J. Proc.*, Vol. 83, 1986, pp. 994-1000.
56. Frearson, J. P. H., "Sulfate Resistance of Combination of Portland Cement and Ground Granulated Blast-furnace Slag", *ACI, SP-91*, 1986, pp. 1495-1524.
57. Mehta, P. K., "Studies on Chemical Resistance of Low Water- Cement Ratio Concretes", *Cem. Concr. Res.*, Vol. 15, 1985, pp. 969-978.
58. Hobbs, D. W., "Influence of Pulverized Fuel Ash and Granulated Blast-furnace Slag Upon Expansion Caused by the Alkali-Silica Reaction", *Mag. Concr. Res.*, Vol. 34, 1982, pp. 83-93.
59. Nixon, P. J., and Gaze, M. E., "The Use of Blast-Furnace Slag to Reduce Expansion Due to Alkali-Aggregate Reaction", *Proc. 5th Int'l Conf. on Alkali-Aggregate Reaction in Concrete*, Cape Town, S. Africa, 1981.
60. Oberholster, R. E., and Westra, W. B., "The Effectiveness of Mineral Admixtures in Reducing Expansion Due to Alkali-Aggregate Reaction with Malmesbury Group Aggregates", *ibid.*, 1981.
61. Searsale, R., and Grigione, G., "On Minimizing the Alkali-Aggregate Reaction: Influence of Powdered Volcanic Tuff, Blast-furnace Slag, and Fly Ash", *Proc. 7th Int'l Conference on Alkali-Aggregate Reaction*, Ottawa, Canada, 1986.
62. Litvan, G. G., and Meyer, A., "Carbonation of Granulated Blast-furnace Slag Cement Concrete During Twenty Years' of Field Exposure", *ACI SP-91*, 1986, pp. 1446-1462.

34 Mehta

63. Vennesland, O., and Gjorv, O. E., "Silica Fume Concrete - Protection Against Corrosion of Embedded Steel", *ibid.*, p. 719.
64. Bamforth, P. B., "In-situ Measurement of the Effects of Partial Portland Cement Replacement Using Fly Ash and Ground Granulated Blast-Furnace Slag, on the Performance of Mass Concrete", *Proc. Inst. of Civil Engr.*, Part 2, 1980, pp. 777-800.
65. Aitcin, P.C., Bedard, C., Plumat, M., and Haddad, G., "Very High Strength Cement for Very High Strength Concrete", *Mat. Res. Soc. Symp.*, *Proc.*, Vol. 42, 1985, pp. 201-210.
66. Virtanen, J., "Freeze-Thaw Resistance of Concrete Containing Blast-furnace Slag, Fly Ash, or Condensed Silica Fume", *ACI SP-79*, 1988, pp. 923-942.
67. Gjorv, O. E., Baerland, T., and Ronning, H. R., "High Strength Concrete for Highway Pavements and Bridge Decks", *Proc. Symp. Utilization of High Strength Concrete*, Stavanger, Norway, 1987, pp. 111-122.
68. Mehta, P. K., "Standard Specifications for Mineral Admixtures", *ACI SP-91*, 1986, pp. 637-658.
69. Manz, O. E., "Proposed Revision to Specifications and Test Methods for Fly Ash for Use in Portland Cement Concrete", *ibid.*, p. 659-680.
70. Hogan, F. J., and Rose, J. H., "ASTM Specification for Ground Iron Blast-furnace Slag", *ibid.*, pp. 1551-1576.
71. Isabelle, H., "The Development of a Canadian Specification for Silica Fume", *ibid.*, pp. 1577-1588.
72. Kreijger, P. C., "Ecological Properties of Building Materials", *Mat. and Structures*, Vol. 20, No. 118, 1987, pp. 248-254.
73. Ravina, D., and Mehta, P. K., "Properties of Fresh Concrete Containing Large Amounts of Fly Ash", *Cem. Conc. Res.*, Vol. 16, No. 6, Nov. 1986, pp. 227-238.
74. Ravina, D., and Mehta, P. K., "Compressive Strength of Low Cement/High Fly Ash Concrete Mixtures", *Cem. Conc. Res.*, Vol. 18, No. 4, July 1988, pp. 571-583.
75. Malhotra, V. M., "Superplasticized Fly Ash Concrete for Structural Applications", *Concrete International*, Vol. 8, No. 12, Dec. 1986, pp. 28-31.
76. Langley, W. S., Carette, G. G., and Malhotra, V. M., "Structural Concrete Incorporating High Volumes of ASTM Class F Fly Ash", *Transportation Board*, Washington, D.C., 67th Meeting, January 1988.

TABLE 1--ANNUAL PRODUCTION AND UTILIZATION RATES
OF SILICEOUS BY-PRODUCTS (TONNES) *

COUNTRY	Fly Ash, x 10 ⁶		Blast-furnace Slag, + x 10 ⁶		Condensed Silica Fume, x 10 ³	
	Production	Utilization	Production	Utilization	Production	Utilization
AUSTRALIA	3.5	0.25	4.7	0.12	60	20
CANADA	3.3	0.8	2.9	0.2	23	11
CHINA	35	7.2	22	16	none	none
DENMARK	1	0.45	none	none	none	none
FRANCE	5.1	1.5	10.4	1.9	60	none
GERMANY FR	2.6	2.0	15	2.8	25	none
INDIA	19	0.5	7.8	2.8	none	none
JAPAN	3.7	0.5	24	8.2	25	none
NETHERLANDS	0.5	0.3	1.1	1	none	none
NORWAY	none	none	0.1	none	140	40
SOUTH AFRICA	12.9	0.1	1.5	0.6	43	0
SWEDEN	0.1	.02	0.1	0.03	10	1
UNITED KINGDOM	13.8	1.3	1.5	0.25	none	none
UNITED STATES	47	5	13	1	100	2

*The production and utilization rates shown in the Table are for the year 1984. The utilization data represents only the amount of material used as a pozzolanic and/or cementitious constituent of hydraulic cements and structural concrete.

+Blast-furnace slag production data include the total quantity of all iron blast-furnace slag including air-cooled slag. The utilization data are for the granulated or pelletized slag consumed by the cement and concrete industries.

TABLE 2--CLASSIFICATION, COMPOSITION, AND PARTICLE CHARACTERISTICS OF SILICEOUS BY-PRODUCTS USED AS CEMENT ADDITIONS, OR AS MINERAL ADMIXTURES IN CONCRETE*

Classification	Chemical and Mineralogical Composition	Particle Characteristics
I. <u>Cementitious</u> Rapidly-cooled blast furnace slag	Mostly silicate glass containing calcium, magnesium, and aluminum. Crystalline compounds of melilite group and merwinite may be present in small quantities.	Unprocessed material is granular or pelletized and contains 5 to 15% moisture. Before use it is dried and ground to particles mostly less than 45 μm (400 to 500 m^2/kg Blaine). Particles have rough texture.
II. <u>Cementitious and Pozzolan</u> High-calcium fly ash ($> 10\%$ CaO)	Mostly silicate glass ⁺ containing calcium, magnesium, and aluminum. The small quantity of crystalline matter present generally consists of quartz and C_3A ; free lime and periclase may be present; CS and $\text{C}_4\text{A}_3\text{S}$ may be present in the case of high-sulfur coals. Unburnt carbon is usually less than 2%.	Powder corresponding to 10-15% particles larger than 45 μm (usually 300-400 m^2/kg Blaine). Most particles are solid and spheroidal with less than 20 μm diameter. Particle surface is generally smooth but not as clean as in low-calcium fly ash.
III. <u>Highly Pozzolan</u> a. Condensed silica fume	Consist essentially of silica in non-crystalline form.	Extremely fine powder consisting of solid and spheroidal particles mostly less than 0.1 μm diameter (about 20000 m^2/kg surface area by nitrogen adsorption).
b. Rice husk ash produced by controlled incineration	Consist essentially of silica in noncrystalline form.	Particles are generally less than 45 μm but they are highly cellular (about 60000 m^2/kg surface area by nitrogen absorption).
IV. <u>Normal Pozzolan</u> Low-calcium fly ash ($< 10\%$ CaO)	Mostly silicate glass containing aluminum, and iron. The small quantity of crystalline matter present consists generally of quartz, mullite, hematite, and magnetite. Unburnt carbon is usually less than 5% but at times may be up to 10%.	Powder corresponding to 15-30% particles larger than 45 μm (usually 250-350 m^2/kg Blaine). Most particles are solid and spheroidal with average 20 μm diameter. Cenospheres and pterospheres may be present.
V. <u>Others</u> a. Slowly-cooled blast furnace slag	Consist essentially of crystalline silicate minerals, and relatively small amount of noncrystalline matter.	The materials must be pulverized to very fine particle size in order to develop satisfactory cementitious or pozzolanic activity. Ground particles are rough in texture.
b. bottom ash, boiler slag, field-burnt rice husk ash.		

*based on P. K. Mehta, Proc. First Int'l Symp. on Fly Ash, Silica Fume, and Slag, Vol. 1, ACI-SP 79, 1983.

+ In fly ashes containing more than 20% CaO, the composition and reactivity of the glass are much different than the glass in low-calcium fly ash; the glass in high-calcium fly ash is more reactive.

TABLE 3--SODIUM SILICATE MODEL GLASS COMPOSITIONS (17)

Na ₂ O %	SiO ₂ %	NBO/Si	Structure	XRD glass max. (^o 2 _θ _{max})	
0	100	0	3d	21.3	-
20	80	-	3d, sheets, chains	22.5	?
30	70	-		24.5	30.4
32	68	-		24.5	31.4
34 ^a	66	1	sheets, chains,	24.5	31.4
36	64	-	monomer	24.5	32.0
38	62	-		24.5	32.5
40	60	-		24.5	32.5
50 ^b	50	2	chains, dimer, monomer	-	34.0

^aNa₂O.2SiO₂ (disilicate)^bNa₂O.SiO₂ (metasilicate)TABLE 4--CHARACTERISTICS OF LEAN CONCRETE
CONTAINING LARGE VOLUMES OF FLY ASH

	Reference (73,74)			Reference (75,76)	
Cement (C), kg/m ³	210	135	120	100	50
Fly ash (F), kg/m ³	--	140	180	125	190
Water (W), kg/m ³	170	150	140	110	112
F/(C+F), ratio	--	0.51	0.60	0.56	0.56
W/(C+F), ratio	0.80	0.55	0.47	0.49*	0.33*
Air content, %	+	+	+	4**	4-6**
Slump, mm	55	55	55	100	40-110
Compressive Strength, MPa					
28-d	15	13	10	23	28-35
90-d	18	20	17	38	40
1-yr.	20	31	32	--	--

+ non air-entrained mixture.

* contains a superplasticizing admixture.

** contains an air-entraining admixture.

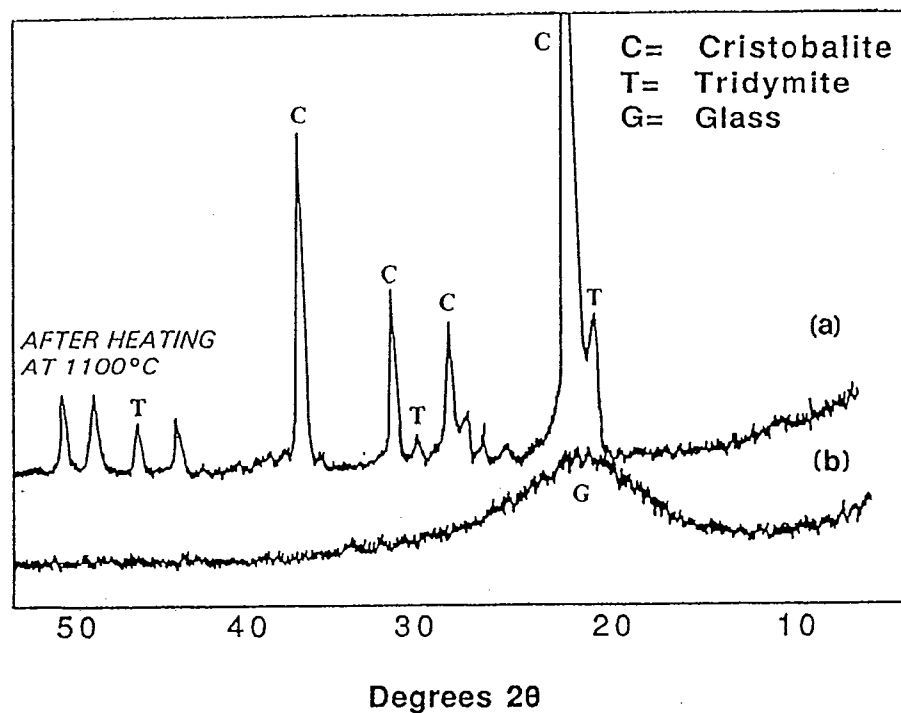


Fig. 1--X-ray diffractograms of (a) crystalline silica, and (b) glassy silica (14)

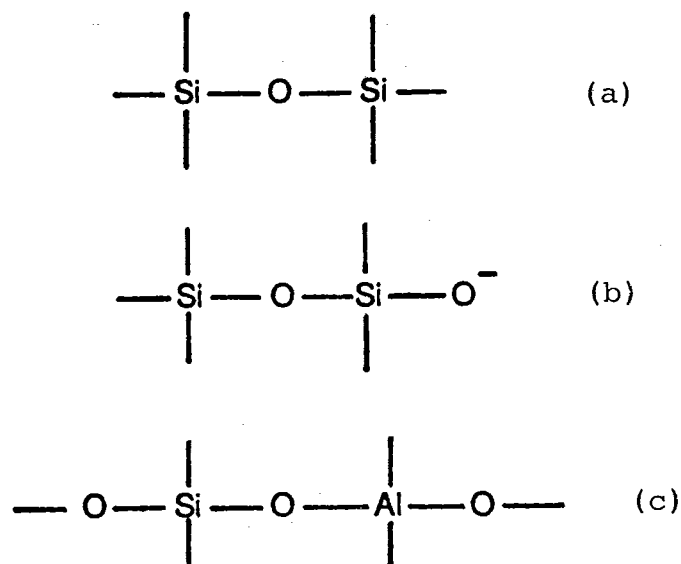


Fig. 2--Structure of silicate glass (14):

- (a) typical Si-O chain with oxygen bridging in simple glasses
- (b) non-bridging oxygens in complex glasses containing Na^+ ions
- (c) random chemical disorder resulting from substitution of Si by Al

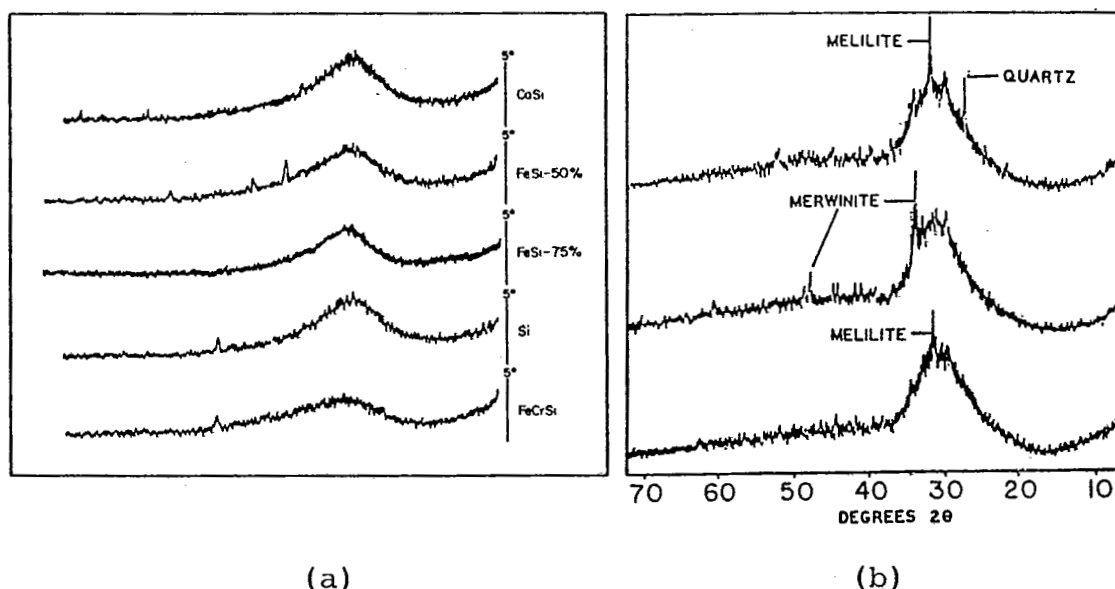


Fig. 3--X-ray diffraction spectra of (a) different samples of condensed silica fume (6), (b) different samples of quenched blast-furnace slag (14)

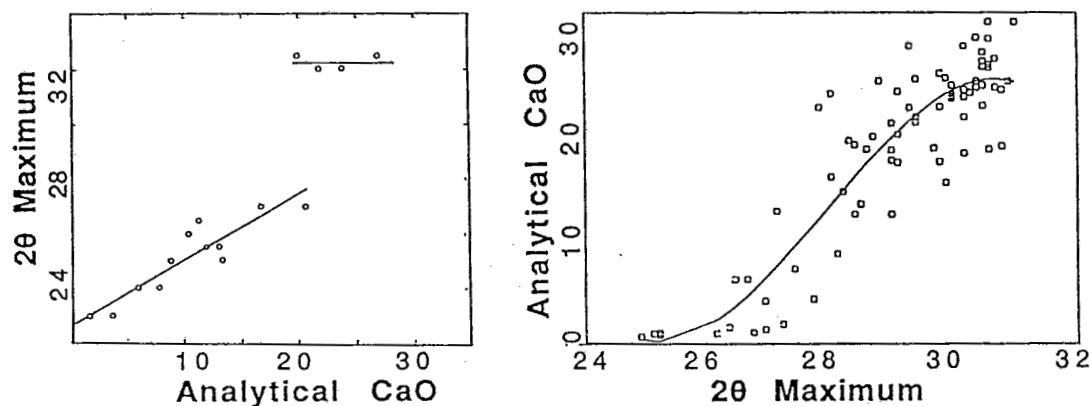


Fig. 4--Variation of XRD glass maxima versus analytical CaO contents for fly ashes: (a) after Diamond (16), (b) after McCarthy et al (19)

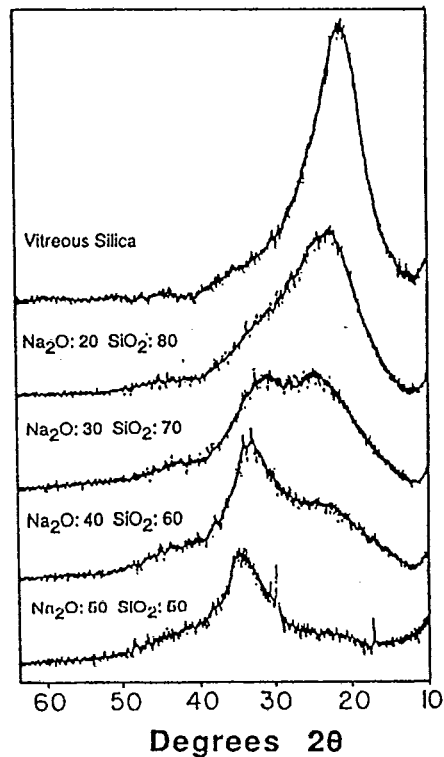


Fig. 5--X-ray diffraction patterns for $\text{Na}_2\text{O-SiO}_2$ model glasses (17)

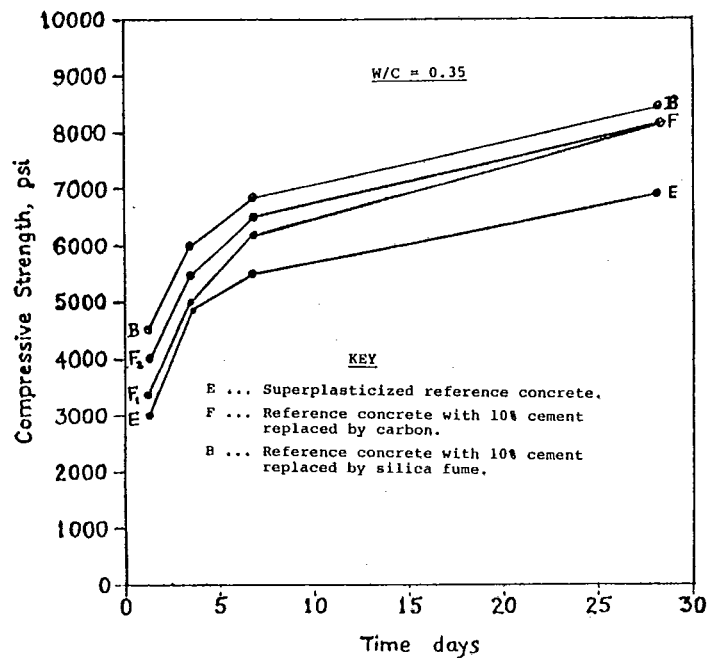


Fig. 6--Effect of pozzolanic or non-pozzolanic fine-particle additions on the compressive strength of concrete (34)

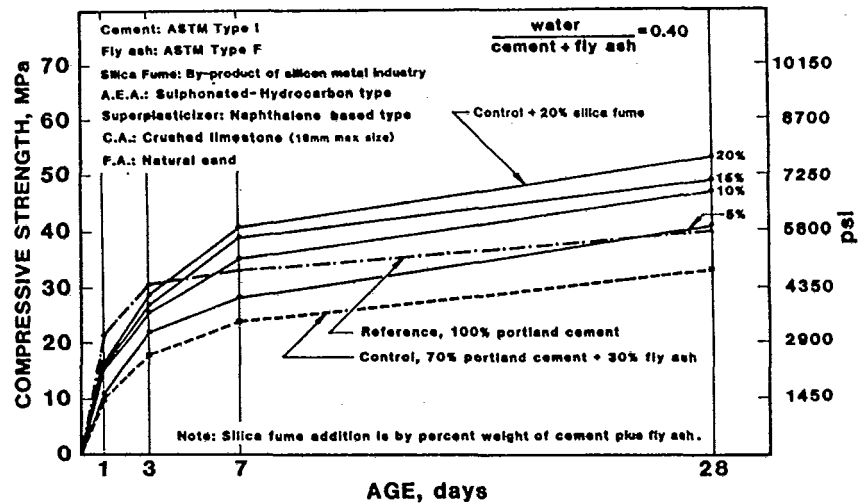


Fig. 7--Compressive strength versus age for fly ash concretes with a $W/(C+F)$ of 0.40, containing various additions of condensed silica fume (38)

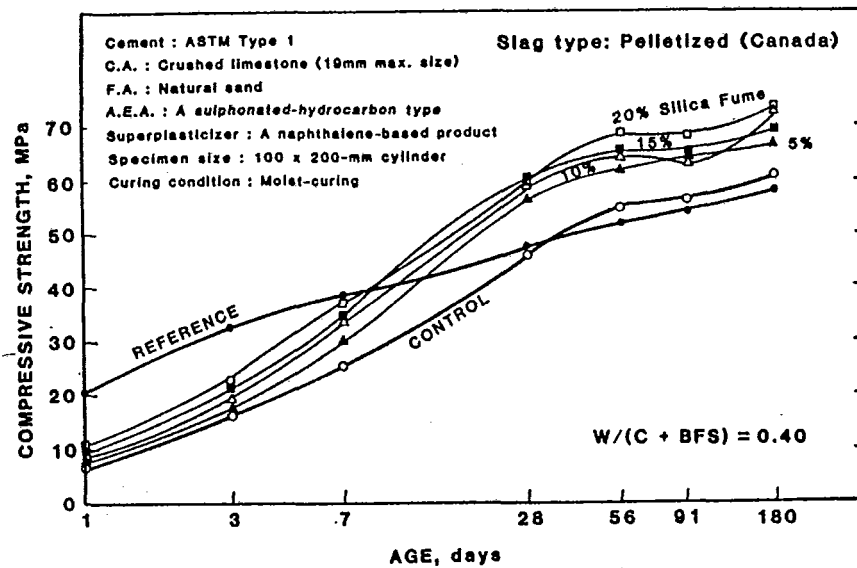


Fig. 8--Age versus compressive strength relationship for concrete incorporating condensed silica fume and pelletized slag; $W/(C+BFS) = 0.40$ (39)

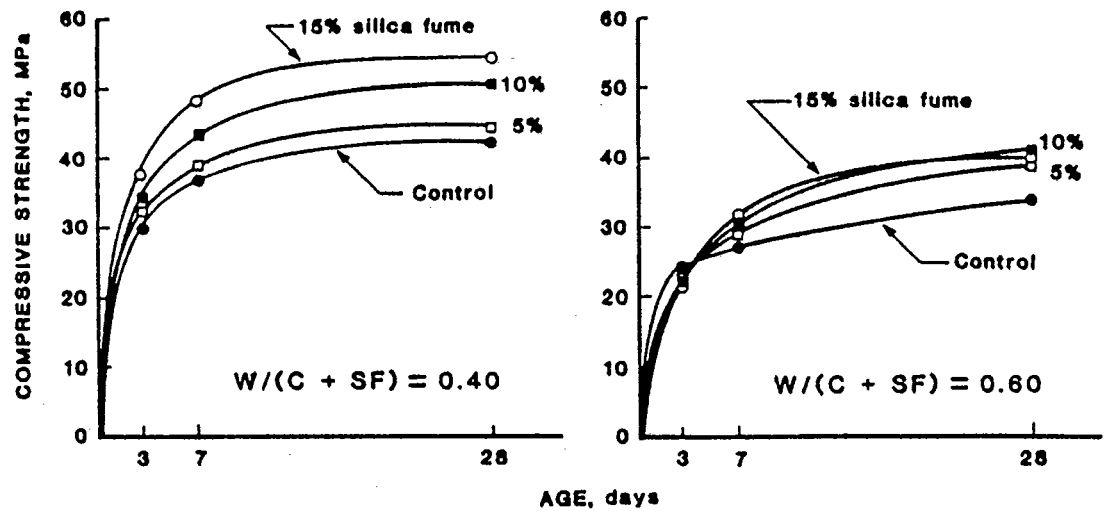


Fig. 9--Compressive strength of silica fume concrete made with W/(C+SF) ratio of 0.4 and 0.6 (41)

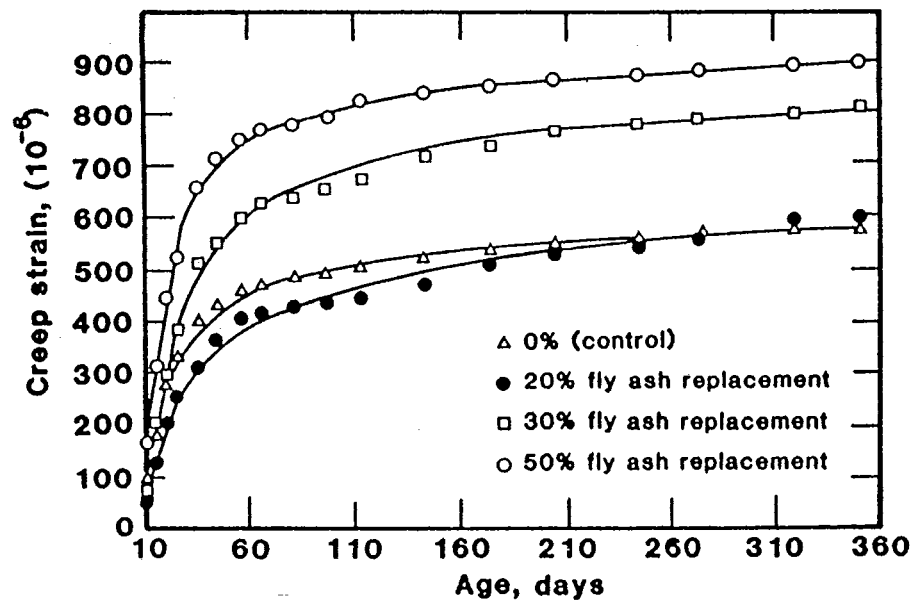


Fig. 10--Creep of fly ash concretes (46)