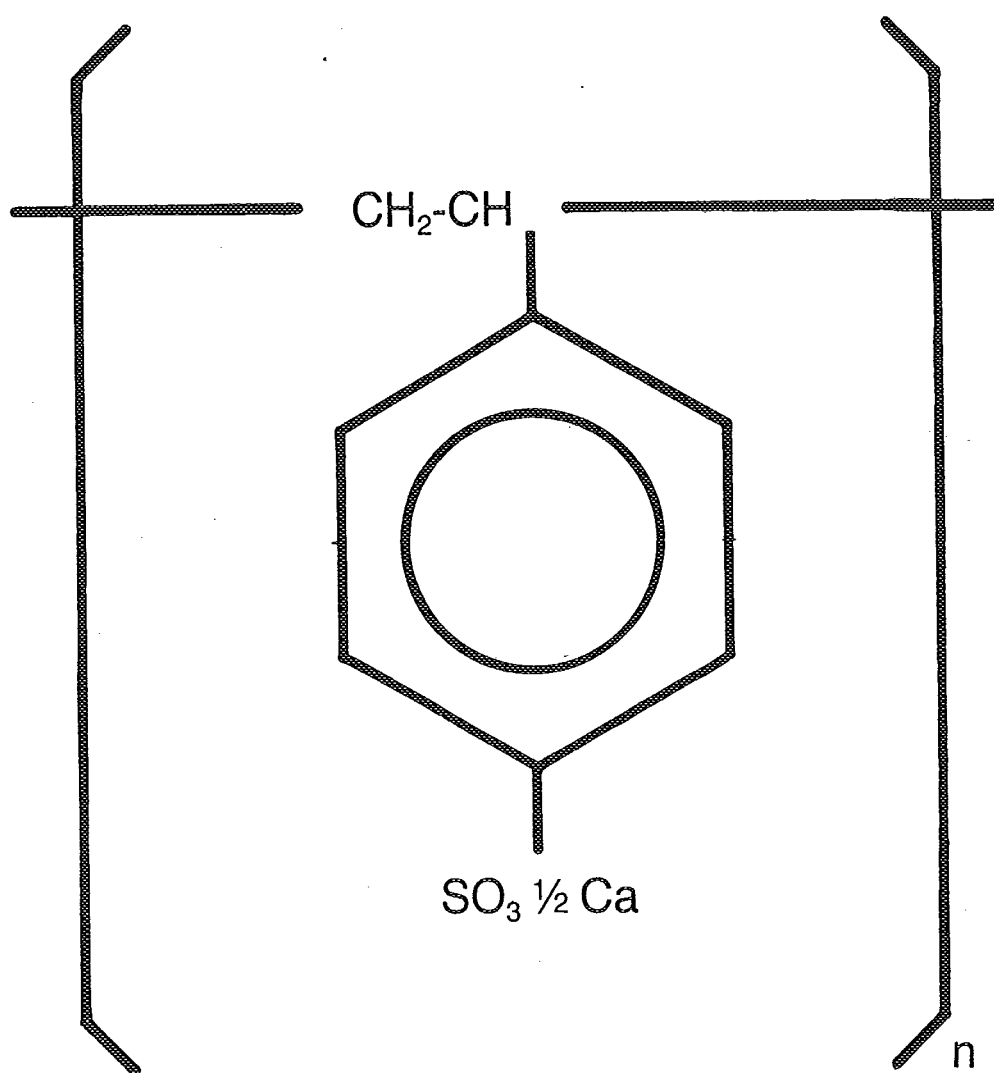


Superplasticizers and Other Chemical Admixtures in Concrete

Proceedings Third International Conference
Ottawa, Canada, 1989



American Concrete Institute, Detroit

V.M. Malhotra
Editor



SP-119
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 June 1, 1990. All discussion approved by the Technical Activities Committee along with closing remarks by the authors will be published in the November-December 1989 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 89-85387

PREFACE

In May, 1978, the Canada Centre for Mineral and Energy Technology (CANMET), in association with the American Concrete Institute, the ACI Eastern Ontario and Quebec Chapter, and the Structural Division of the Canadian Society for Civil Engineering, sponsored a three-day conference in Ottawa on the use of superplasticizers in concrete. Selected papers from the symposium were published as American Concrete Institute special publication SP-62.

In 1981, CANMET in association with the above organizations, sponsored a second three-day international conference in Ottawa on the use of superplasticizers in concrete. The proceedings of the conference were published as American Concrete Institute special publication SP-68.

In October 1989, CANMET in association with the American Concrete Institute and the ACI Eastern Ontario and Quebec Chapter sponsored the third three-day international conference in Ottawa. The purpose of the third conference was to review the progress made since the meetings in 1978 and 1981; and to bring together representatives of the chemical admixtures, cement, and concrete industries to exchange information and to delineate new areas of needed research. The scope of this conference was expanded to include chemical admixtures other than superplasticizers. The proceedings of the conference were published as American Concrete Institute special publication SP-119.

A total of 48 papers from more than 15 countries were received and reviewed by an expert panel of ACI reviewers, and 33 were accepted for publication. The cooperation of the authors in accepting the reviewers' suggestions and in revising their manuscripts is greatly appreciated.

Particular thanks are extended to the members of the review panel for their contributions toward the publication of this volume.

V.M. Malhotra, Editor
Chairman, Third CANMET/ACI

International Conference on Superplasticizers
and Other Chemical Admixtures in Concrete

ORGANIZING COMMITTEE

Third International Conference on
Superplasticizers and Other Chemical Admixtures in Concrete

Ottawa, Canada
October 1989

* * * * *

V.M. Malhotra
Chairman

Theodore W. Bremner (member)
Georges G. Carette (member)

Henri L. Isabelle (member)
V.S. Ramachandran (member)

Harry S. Wilson
Secretary-Treasurer

CONTENTS

PREFACE.....	iii
SUPERPLASTICIZERS: A GLOBAL REVIEW WITH EMPHASIS ON DURABILITY AND INNOVATIVE CONCRETES by V.M. Malhotra.....	1
REUSE OF RETURNED CONCRETE BY HYDRATION CONTROL: CHARACTERIZATION OF A NEW CONCEPT by F.D. Kinney.....	19
CASE HISTORIES -- THE USE OF SUPERPLASTICIZERS IN TWO EXTREMES OF CONCRETE PLACEMENT DIFFICULTIES by A.J. Hulshizer, J.J. Ucciferro, and G.E. Gray.....	41
PROPERTIES OF HIGH-STRENGTH CONCRETE WITH SILICA FUME USING HIGH-RANGE WATER REDUCER OF SLUMP RETAINING TYPE by K. Mitsui, H. Kasami, Y. Yoshioka, and M. Kinoshita....	79
CHEMICAL CHARACTERIZATION OF PLASTICIZERS AND SUPERPLASTICIZERS by E. Ista and A. Verhasselt.....	99
PHYSIOCHEMICAL CHARACTERIZATION OF SUPERPLASTICIZERS by J. Khorami and P.-C. Aitcin.....	117
RAPID METHODS OF DISTINGUISHING PLASTICIZER FROM SUPERPLASTICIZER AND ASSESSING SUPERPLASTICIZER DOSAGE by A. Verhasselt and J. Pairon.....	133
RELATIVE EFFECTS OF Ca-POLYSTYRENE SULFONATE AND Na-SULPHONATE-BASED SUPERPLASTICIZERS ON PROPERTIES OF FLOWING CONCRETE by Y. Sekiguchi, T. Okada, and T. Ukigai.....	157
RHEOLOGICAL BEHAVIOR OF PORTLAND CEMENT IN THE PRESENCE OF A SUPERPLASTICIZER by E. Hanna, K. Luke, D. Perraton, and P.-C. Aitcin.....	171
EFFECT OF CHEMICAL ADMIXTURES ON THE RHEOLOGY OF FRESH CONCRETE DURING VIBRATION by S. Kakuta and T. Kojima.....	189
INFLUENCE OF DIFFERENT SULFONATED NAPHTHALENE POLYMERS ON THE FLUIDITY OF CEMENT PASTE by F. Basile, S. Biagini, G. Ferrari, and M. Collepardi.....	209
EFFECT OF WATER DISPERSIBLE POLYMERS ON THE PROPERTIES OF SUPERPLASTICIZED CEMENT PASTE, MORTAR, AND CONCRETE by J.J. Beaudoin and V.S. Ramachandran.....	221

SLUMP CONTROL WITH REACTIVE POLYMERIC DISPERSANT by T. Izumi, T. Mizunuma, M. Iizuka, and M. Fukuda.....	243
INTERACTION OF POLYMER WITH CALCIUM HYDROXIDE AND CALCIUM TRISILICATE by S. Chandra and P. Flodin.....	263
EFFECT OF RETEMPERING WITH SUPERPLASTICIZER ON PROPERTIES OF FRESH AND HARDENED CONCRETE MIXED AT HIGHER AMBIENT TEMPERATURES by M.A. Samarai, V. Ramakrishnan, and V.M. Malhotra.....	273
AIR-VOID CHARACTERISTICS AND FREEZING AND THAWING RESISTANCE OF SUPERPLASTICIZED AIR-ENTRAINED CONCRETE WITH HIGH WORKABILITY by E. Siebel.....	297
DEVELOPMENT OF ADMIXTURES FOR HIGHLY DURABLE CONCRETE by Y. Ohama, K. Demura, Y. Satoh, K. Tachibana, and Y. Miyazaki.....	321
A MODEL FOR DEICER SCALING RESISTANCE OF FIELD CONCRETES CONTAINING HIGH-RANGE WATER REDUCERS by D. Whiting and J. Schmitt.....	343
SUPERPLASTICIZERS AND CONCRETE DURABILITY by R.N. Swamy.....	361
USE OF CONCRETE ADMIXTURES TO PROVIDE LONG-TERM DURABILITY FROM STEEL CORROSION by N.S. Berke and L.R. Roberts.....	383
EFFECT OF ALKALI SULFATE ON THE RHEOLOGICAL BEHAVIOR OF CEMENT PASTE CONTAINING A SUPERPLASTICIZER by T. Nawa, H. Eguchi, and Y. Fukaya.....	405
OPTIMIZATION OF SUPERPLASTICIZER TYPE AND DOSAGE IN FLY ASH AND SILICA FUME CONCRETES by M. Collepardi, S. Monosi, and M. Valente.....	425
A STUDY ON SUPERPLASTICIZED CONCRETE CONTAINING HIGH VOLUMES OF BLAST-FURNACE SLAG by S. Nishibayashi, A. Yoshino, S. Hideshima, M. Takada, and T. Chikada.....	445
COMBINED EFFECT OF SUPERPLASTICIZER AND ACRYLIC LATEX IN CEMENT MORTARS WITH AND WITHOUT SILICA FUME by C. Atzeni, G. Mantegazza, L. Massidda, and U. Sanna...	457
CONSTRUCTION OF A DRY DOCK USING TREMIE SUPERPLASTICIZED CONCRETE by M. Collepardi, R. Khurana, and M. Valente.....	471

EFFECTS OF CHEMICAL ADMIXTURES ON COLLOIDAL UNDERWATER CONCRETE by M. Kawakami, S. Wada, and K. Suzukawa.....	493
USE OF CHEMICAL ADMIXTURES IN CONCRETE PLATFORMS by H. Ronneberg.....	517
A YEAR-ROUND ACCELERATING ADMIXTURE by J.W. Brook and R.J. Ryan.....	535
NEW DEVELOPMENTS IN SUPERPLASTICIZERS FOR LIGHTWEIGHT CONCRETE by M. Berra, G. Ferrara, G. Mantegazza, and A. Sereni....	557
EFFECT OF SUPERPLASTICIZER AND VISCOSITY-INCREASING ADMIXTURE ON PROPERTIES OF LIGHTWEIGHT AGGREGATE CONCRETE by T. Kawai and T. Okada.....	583
FIELD TRIALS OF SUPERPLASTICIZED GROUT AT AECL's UNDERGROUND RESEARCH LABORATORY by M.N. Gray and L.D. Keil.....	605
EVALUATION OF SUPERPLASTICIZERS IN CONCRETE by P.K. Mukherjee.....	625
ADSORPTION STUDIES OF ³⁵ S-LABELLED SUPERPLASTICIZER IN CEMENT-BASED GROUT by M.N. Onofrei and M.N. Gray.....	645
SI (Metric) TABLES.....	661
INDEX.....	663

SP 119-1

Superplasticizers: A Global Review with Emphasis on Durability and Innovative Concretes

by V.M. Malhotra

Synopsis: This review paper traces the development of superplasticizers in Japan and Germany, describes briefly their mode of action, and discusses the properties of superplasticized fresh and hardened concrete. Data are presented on the use of superplasticizers in Australia, Canada, Japan, Singapore, U.K., U.S.A. and Western Europe. The performance of superplasticized concrete under freezing and thawing conditions both in the laboratory and in the field is discussed, and the use of superplasticizers in the development of innovative concretes is described. The ASTM and Canadian specifications dealing with superplasticizers are discussed, and the paper is concluded with a list of pertinent references.

Keywords: admixtures; concretes; fiber-reinforced concretes; fly ash; freeze-thaw durability; performance; plasticizers; reviews; shotcrete; silica fume; water-reducing agents

2 Malhotra

ACI Hon. Member V.M. Malhotra is Head, Concrete Technology Section, CANMET, Energy, Mines and Resources Canada, Ottawa, Canada. Dr. Malhotra has published numerous technical papers and reports in the area of concrete technology and supplementary cementing materials. He was Chairman of the First and Second CANMET/ACI International Conferences on Superplasticizers in Concrete, held in Ottawa in 1978 and 1981.

INTRODUCTION

Historically, lignosulphonates have formed the basis of water-reducing admixtures in the U.S.A. and elsewhere, since the early 1940's. However, research in the early 1960's in Japan and Germany led to the development of superplasticizers (high-range water-reducing admixtures). In Japan, Hattori and co-workers (1) pioneered the development of formaldehyde condensates of beta-naphthalene sulfonates with the primary aim of significantly reducing the water demand of concrete admixtures in order to produce high-strength concrete. Water reductions of up to 30 per cent were achieved with the use of one type of superplasticizer. This admixture was introduced into the Japanese market in 1964 and since then, it has gained considerable acceptance in the concrete industry. In Germany, Aignesberger and his colleagues (2) developed the melamine based superplasticizer with the primary aim of producing what is now known as "flowing concrete". The admixture was introduced into the German market in the early 1970's.

The first known use of superplasticizers in North America was in 1975 when melamine-based admixtures were used in the fabrication of large precast concrete units of the Montreal Olympic Stadium which is an outstanding example of segmental concrete construction (3).

The First and Second CANMET/ACI International Conferences on the Development and Use of Superplasticizers in Concrete were held in Ottawa, Canada in 1978 and 1981, respectively. These conferences gave considerable impetus to the use of superplasticizers in Canada, the USA and other countries (4,5).

This paper gives a global review of the use of superplasticizers in concrete. The performance of superplasticized concrete in a freezing and thawing environment, and the role of superplasticizers in the development of innovative concretes is given special emphasis, because other properties of fresh and hardened concrete are adequately discussed in various publications (4,5).

CLASSIFICATION OF SUPERPLASTICIZERS

Superplasticizers may be classified into the following four categories:

1. Sulphonated melamine-formaldehyde condensate
2. Sulphonated naphthalene-formaldehyde condensate
3. Modified lignosulphonates
4. Other superplasticizers such as sulphonic-acid esters, carbohydrate esters, etc.

Significant variations exist in each of the above four categories. The molecular weight of the superplasticizers may vary from less than 100 to 100,000 (6).

MODE OF ACTION

It is generally agreed that the action of superplasticizers is primarily due to their being adsorbed on cement particles and exerting an electrostatic repulsion. This results in the dissociation of the cement agglomerates into primary particles with a significant decrease in the viscosity of the cement/water/superplasticizer system. Superplasticizers may also contribute to the decrease in the surface tension of water and to producing lubricating films at particle surfaces (7). An in-depth study of the rheology, adsorption, hydration and zeta potential characteristics of cement paste and mortars provides a better understanding of the role of superplasticizers in cementitious systems (6).

EFFECTS OF SUPERPLASTICIZERS ON THE PROPERTIES OF FRESH AND HARDENED CONCRETE

Considerable data have been published on the properties of fresh and hardened superplasticized concrete (4,5,8) and a detailed discussion is beyond the scope of this paper. However, some significant properties of fresh and hardened superplasticized concrete are described below.

Properties of Fresh Concrete

There is no undue segregation or bleeding of concrete incorporating superplasticizers when proper concrete mixture proportions and correct dosages of superplasticizers are used. The setting time of superplasticized concrete is sometimes delayed, especially when lignosulphonate-based superplasticizers are used, but this is of no serious consequence in concrete operations.

4 Malhotra

The entrained-air content of fresh superplasticized concrete may show some decrease with time. It, therefore, may be important that air content of fresh concrete be determined immediately after mixing, and before casting test specimens.

The large increases in slump of the superplasticized concrete are of short duration, and within 30 to 60 minutes the concrete reverts back to its original slump. This problem can generally be overcome by the use of a retarded version of the superplasticizers and the use of repeated dosages of the admixture (9).

Properties of Hardened Concrete

The increase in the mechanical properties, i.e., compressive and flexural strengths and modulus of elasticity, is generally commensurate with reductions in water content when superplasticizers are used as high-range water-reducers (8). Compressive strengths approaching 100 MPa with corresponding increase in flexural strength and modulus of elasticity have been achieved with the use of superplasticizers. The use of silica fume is not essential in superplasticized concrete if the compressive strength requirement is in the order of 80 MPa.

The general consensus appears to be that concrete incorporating superplasticizers has approximately the same shrinkage and creep as the reference concrete, though there are exceptions (8).

WORLDWIDE USE OF SUPERPLASTICIZERS

Since their introduction in the early 1960's in Japan, and in the early 1970's in Germany, the use of superplasticizers has increased dramatically in Japan and several countries in Europe. Superplasticizers are also being used increasingly in developing countries and eastern Europe where indigenous products have been developed. In North America, the acceptance of superplasticizers was slow in the beginning. This was due primarily to conservatism of the construction industry and marketing problems experienced by the Japanese and the European manufacturers. This was further compounded by the fact that initial investigations performed by the Corps of Engineers, U.S.A, indicated poor performance of superplasticized concrete in rapid freezing and thawing tests conducted in accordance with ASTM C 666 Procedure A (10). Lately, both the technical and marketing issues referred to above have been resolved, and the use of superplasticizers is on the increase in North America. Table 1 provides some data on the current usage of superplasticizers by the ready-mixed and precast concrete industry in various countries. The very low usage of superplasticizers in France and the U.K. is worth noting.

DURABILITY OF CONCRETE INCORPORATING SUPERPLASTICIZERS

Soon after superplasticizers had been introduced into North America, questions were raised as to the freezing and thawing durability of concrete incorporating these new admixtures, both in the rapid freezing and thawing tests, and in in-place concrete (10). It is now recognized that although the bubble spacing factor ($\bar{L}$) of superplasticized concrete may exceed the established limit of 0.2 mm, this in no way impairs the durability of the superplasticized concrete (11).

Durability of Superplasticized Concrete in Laboratory Rapid Freezing and Thawing Tests

CANMET has been investigating the durability of air-entrained superplasticized concrete using ASTM test method C 666 Procedure A (rapid freezing in water and thawing in water). These investigations have led to the following conclusions (11).

Non-Air-Entrained Concrete

Non-air-entrained concrete prisms, regardless of the water-to-cement ratio, when tested in accordance with ASTM C 666 Procedure A (freezing in water and thawing in water) show very low durability factors (<31).

Non-air-entrained concrete prisms with water-to-cement ratios of 0.50 to 0.70 show very low durability factors (<12) when tested in accordance with ASTM C 666 Procedure B (freezing in air and thawing in water). However, concrete prisms with a water-to-cement ratio of 0.35 show satisfactory resistance to 300 cycles of freezing and thawing (durability factor >90). Between 300 and 400 cycles the prisms deteriorate markedly. Notwithstanding the strength loss associated with air entrainment, the use of air-entrained concrete is recommended for low water-to-cement ratio concrete for added assurance against damage when concrete is to be subjected to repeated cycles of freezing and thawing.

Air-Entrained Concrete

Regardless of the water-to-cement ratio used, the air-entrained concrete prisms show high durability factors (>90) at the end of 300 cycles of freezing and thawing. This is true for both ASTM C 666 Procedures A and B. However, beyond 300 cycles of freezing and thawing, concrete prisms with a water-to-cement ratio of 0.70 seem to perform poorly in test Procedure A as compared with test Procedure B.

6 Malhotra

Air-Entrained Superplasticized Concrete

The bubble spacing factors L for air-entrained superplasticized concrete are, in some cases, higher than 0.20 mm. But in spite of the higher values of L , and regardless of the test procedure used, the durability factors for concretes are high (>90) at the end of 300 cycles of freezing and thawing for concrete mixes of Series I*, and at the end of more than 700 cycles of freezing and thawing for concrete mixes of Series II**. These durability factors are compatible with those for non-superplasticized air-entrained concrete.

Durability of In-Place Superplasticized Concrete

Under the U.S.A National Co-operative Highway Research Program (NCHRP) project 10-32, "Durability of In-Place Concrete Containing High-Range Water-Reducing Admixtures", Construction Technology Laboratories, Inc., Skokie, U.S.A, conducted a study of concrete placed with high-range water reducing admixtures (12). Existing concrete bridges and highway pavement and cores from these structures were examined to assess the relationship between durability and air-void characteristics. Although these admixtures have not been in use for very long, the study identified factors that appear to influence the production of high quality durable concrete. The authors of the above study concluded that:

1. "High-range water-reducing (HRWR) admixtures, in themselves, have no significant deleterious effects on the surface durability of portland cement concrete exposed to freeze-thaw environments and deicing agents. Behaviour in these environments is similar to "control" concretes prepared without HRWR admixtures.
2. Those qualities that lead to durable conventional concretes also apply to concretes containing HRWR. Properly air-entrained, low w/c ratio concretes that are workable and easy to finish will, in general, be durable even under severe environmental conditions. Factors that impact negatively upon these qualities, such as additions of water at the job site, difficulty in consolidation, overfinishing, or other poor construction practices, will result in a concrete of questionable durability, with or without the inclusion of HRWR.

*Series I concrete mixtures incorporated a melamine-based superplasticizer and **Series II concrete mixtures incorporated a naphthalene-based superplasticizer.

3. Those variables having the greatest effects on scaling of concrete surfaces in this study include the w/c ratio of the concrete, the proportional amount of entrained air removed from the surface zone, and the spacing factor, $\bar{L}$, in the concrete as a whole.
4. By themselves, characteristics of the air-void system in concrete, as measured by standard (ASTM C 457) and novel techniques, show little correlation with durability of concrete surfaces. Although spacing factors and specific surfaces in many HRWR concretes fail to meet minimum guidelines established by the American Concrete Institute, other factors, namely the w/c ratio and amount of entrained air removed from the near surface zone, have a greater influence on durability than do air-void characteristics measured in the bulk of the concrete."

SPECIALIZED INNOVATIVE APPLICATIONS OF SUPERPLASTICIZERS IN CONCRETE

The availability of superplasticizers has led to the development of innovative concretes for specialized applications. Some of these concretes are described below.

Superplasticized High-Volume Fly Ash Concrete

Superplasticized high-volume fly ash concrete for structural applications is relatively a new material. In 1985, CANMET commenced work on the development of the above type of concrete and in these investigations an ASTM Class F fly ash was used in proportions of 50 to 60 per cent of the total cementitious material (13). Low unit water content ($<115 \text{ kg/m}^3$) and a high degree of workability were obtained by the use of high dosages of superplasticizers. This type of concrete had very low water-to-cementitious materials ratio (<0.35), adequate early-age compressive strength ($>9 \text{ MPa}$ at one day), very high later-age strength ($>60 \text{ MPa}$ at one year), very low permeability (<500 coulombs in rapid chloride ion permeability test), and satisfactory resistance to freezing and thawing in ASTM C 666 Procedure A test method. Because of its low cost, very low permeability, and very low heat of hydration, this material offers excellent scope for use in a variety of applications such as thick retaining walls, bridge piers and mass concrete.

Steel or polypropylene fibers can be incorporated in high-volume fly ash concrete to give it added versatility.

8 Malhotra

Superplasticized High-Strength Silica-Fume Concrete

Superplasticized silica-fume concrete is being used increasingly for repairs of structures where impermeability of concrete is of paramount importance (14). This type of air-entrained concrete incorporates 400 to 500 kg/m³ of cement, and 8 to 10% silica fume and moderate dosages of superplasticizer to keep the water-to-cementitious materials ratio to about 0.30. These concretes have high compressive strength (>70 MPa at 28 days) and very high resistance to the penetration of chloride ions (<500 coulombs in rapid chloride ion permeability test).

Superplasticized Fibre-Reinforced Concrete

The incorporation of steel or polypropylene fibres in concrete reduces greatly its workability. This has been one of the serious drawbacks of fibre-reinforced concrete. The incorporation of superplasticizers in fibre-reinforced concrete overcomes this problem of reduced slump, and has led to the increasing acceptance of superplasticized fibre-reinforced concrete, especially for the repair and rehabilitation of deteriorated concrete structures. Fig. 1 shows the concrete piles at Saint John's harbour before and after repair using superplasticized steel fibre-reinforced concrete. The mixture proportions of the air-entrained concrete were as follows (15):

Cement CSA Type 50 (ASTM Type V)	415 kg/m ³
Fly Ash ASTM Class F	105 kg/m ³
Natural Sand	880 kg/m ³
Coarse Aggregates (10 mm max.)	665 kg/m ³
Collated Steel Fibres	74 kg/m ³
(Length 50 mm)	
(Diam. 0.5 mm)	
Specified 28-day Compressive Strength	41.4 MPa
A.E.A.	800 mL/m ³
Superplasticizer	6 L/m ³
Water/Cementitious	0.40

Superplasticized Heavy-Weight Concrete

Superplasticizers have been successfully used to increase the density of heavy-weight concretes by reducing the amount of water and lowering the water-to-cement ratio*.

Superplasticized Fibre-Reinforced Shotcrete

The mixture proportions for wet-mix superplasticized fibre-reinforced shotcrete are similar to those of the superplasticized fibre-reinforced concrete described above,

*CANMET Unpublished Data

except that the "shotcreting" method of placing concrete is used. The fibres can be either of steel or polypropylene depending on the job requirements. The fibres are added to the shotcrete to improve ductility and energy absorption (toughness and impact resistance). The fibres can also be used to control thermal and drying shrinkage cracking (16). Fig. 2 shows the repairs of a harbour berth base using wet shotcrete. Typical mixture proportions and properties for wet-mix superplasticized shotcrete are as follows (16).

Normal Portland Cement (Type 10)	400 kg/m ³
Silica Fume	56 kg/m ³
10 mm Coarse Aggregate (SSD)	460 kg/m ³
Concrete Sand (SSD)	1100 kg/m ³
Water	180 kg/m ³
Water-Reducing Admixture	2 L/m ³
Superplasticizer	7 L/m ³
30 mm Steel Fibre	60 kg/m ³
Air-Entraining Admixture As required for	
Air Content (in place)	7 ± 1%
Slump	80 ± 20 mm
Minimum 28-Day Compressive Strength	40 MPa

NATIONAL STANDARDS ON SUPERPLASTICIZERS

Several countries including Canada and the U.S.A have issued specifications for the use of superplasticizers in concrete. Canadian Standard CAN3-A266.6-M85 covers the use of superplasticizers for both water-reduced and flowing concrete; ASTM C 494 and C 1017 deal with the use of superplasticizers in water-reduced and flowing concretes, respectively. Both of these specifications have requirements for minimum durability factors; the Canadian specification goes further and even recognizes the fact that with air-entrained superplasticized concretes, the bubble spacing factor ($\bar{L}$) can exceed 0.20 mm, a limit which is ordinarily specified for air-entrained concrete.

Tables 2 and 3 give physical requirements for the use of superplasticizers in concrete according to CAN3-A266.6-M85, ASTM C 494 and C 1017. ASTM C 494 defines high-range water-reducing admixture as an admixture that reduces the quantity of mixing water required to produce concrete of a given consistency by 12% or greater. Because of the availability of more efficient high-range water-reducing admixtures in recent years, ASTM should consider revising the above value to 20% or greater.

10 Malhotra

OUTSTANDING ISSUES STILL TO BE RESOLVED

When superplasticizers were introduced in North America, immediate concerns were the loss of workability of superplasticized concrete after about 20 minutes, and the potential durability of such concrete under freezing and thawing conditions. During the intervening years, these issues appear to have been resolved. The loss of workability can be overcome by the use of retarded versions of the products, or by the use of repeated dosages.

As mentioned earlier, the durability of superplasticized concrete is no longer a contentious issue. The problems that still need to be resolved include compatibility of superplasticizers with different types of cements, supplementary cementing materials and other admixtures, the role of alkalies and SO_3 , and the possible loss of bond between structural steel and superplasticized concrete in structural slabs. Rapid quality control methods to check uniformity of superplasticizers are needed. It is hoped that the research currently being undertaken by various institutes will lead to the resolution of these issues in the near future.

CONCLUDING REMARKS

The development and use of superplasticizers has revolutionized the manner in which concrete is being transported, placed and compacted. High-strength concretes having compressive strength exceeding 70 MPa at 28 days are being routinely made using the new admixtures.

The judicious use of superplasticizers has led to the development of innovative concretes such as high-volume fly ash concrete, superplasticized fibre-reinforced concrete and shotcrete and high-strength silica-fume concrete with very low permeability.

Problems associated with the loss of workability with time, and the freezing and thawing durability of the superplasticized concrete have been primarily resolved. Research is needed to resolve other issues such as compatibility between the superplasticizers and various types of cements and supplementary cementing materials. Rapid methods to control quality of the superplasticizers are needed.

In 1980, the writer had concluded an ACI paper with the following statement (8).

"There have been very few major developments in concrete technology in recent years. The concept of air entrainment in the 1940's was one - it revolutionized concrete

technology in North America. It is believed that development of superplasticizers is another major breakthrough which will have a very significant effect on the production and use of concrete in years to come".

The above statement is equally true today, and there is no reason to conclude otherwise.

REFERENCES

1. Hattori, K., "Experiences with Mighty Superplasticizers in Japan"; ACI Special Publication SP-62, 1979, pp. 37-66.
2. Aignesberger, A. and Kern, A., "Use of Melamine-Based Superplasticizer as a Water Reducer", ACI Special Publication SP-68, 1981, pp. 61-80.
3. Holbek, K. and Skrastins, J.I., "Some Experience With the Use of Superplasticizers in the Precast Concrete Industry in Canada", ACI Special Publication SP-62, 1981, pp. 87-100. (Editor: V.M. Malhotra).
4. Malhotra, V.M. (Editor), "Superplasticizers in Concrete"; ACI Special Publication SP-62, 1979, 426 pp.
5. Malhotra, V.M. (Editor), "Developments in the Use of Superplasticizers"; ACI Special Publication SP-68, 1981, 559 pp.
6. Ramachandran, V.S. and Malhotra, V.M., "Superplasticizers"; Chapter 4 in Concrete Admixtures Handbook, 1981, pp. 211-264. (Editor: V.S. Ramachandran).
7. Meyer, A., "Experiences in the Use of Superplasticizers in Germany"; ACI Special Publication SP-62, 1979, pp. 21-36.
8. Malhotra, V.M., "Superplasticizers: Their Effect on Fresh and Hardened Concrete"; ACI Concrete International, Vol. 3, No. 5, May 1981, pp. 66-81.
9. Malhotra, V.M., "Effect of Repeated Dosages of Superplasticizers on Workability, Strength and Durability of Concrete"; CANMET Division Report MRP/MSL 78-40 (OP&J), Energy, Mines and Resources Canada, Ottawa, 1978.
10. Mather, B., "Tests of High-Range Water-reducing Admixtures"; ACI Special Publication SP-62, 1979, 157-166 pp. (Editor: V.M. Malhotra).

12 Malhotra

11. Malhotra, V.M., "Mechanical Properties and Freezing and Thawing Resistance of Non Air-Entrained, Air-Entrained, and Air-Entrained Superplasticized Concrete Using ASTM Test C 666, Procedures A and B"; ASTM Cement, Concrete and Aggregates, Vol. 4, No. 1, 1982, pp. 3-23.
12. Whiting, D. and Schmitt, J., "Durability of In-Place Concrete Containing High-Range Water Reducing Admixtures"; NCHRP Report 296, TRB, Washington, D.C., 1987, 63 pp.
13. Malhotra, V.M., "Superplasticized Fly Ash Concrete for Structural Applications"; ACI Concrete International, Vol. 8, No. 12, 1986, pp. 28-31.
14. Fidjest 1, Per, "Use of Condensed Silica Fume Concrete in Scandinavia"; Paper No. 2, Proceedings, International Workshop on Condensed Silica Fume in Concrete, Montreal, Canada, 1987.
15. Khanna, J., Gilbride, P. and Whitcomb, R., "Steel Fiber-Reinforced Concrete Jackets for Repairing Concrete Piles"; ACI Special Publication SP-109, 1988, pp. 227-252. (Editor: V.M. Malhotra).
16. Gilbride, P., Morgan, D.R. and Bremner, T.W., "Deterioration and Rehabilitation of Berth Faces in Tidal Zones at the Port of Saint John"; ACI Special Publication SP-109, 1988, pp. 199-226 (Editor: V.M. Malhotra).

TABLE 1--WORLDWIDE USE OF SUPERPLASTICIZERS IN THE
READY-MIXED AND PRECAST CONCRETE INDUSTRY

Country	Ready-mixed Concrete		Precast Concrete (not including pipes and poles etc.)	
	Annual Production, m ³ x 10 ⁶	% incorporating superplasticizers	Annual Production, m ³ x 10 ⁶	% incorporating superplasticizers
Australia ¹	15	1	0.25	20 to 30
Canada ²	26	4 to 5	--	--
France ³	28	<1	--	--
Italy ⁴	60	10	--	25
Japan ⁵	--	9.7	--	100
Netherlands ⁶	--	10	--	20
Singapore ⁷	3	15 to 20	--	800 tons
Norway ⁸	2.8	2000 tons	≈1	45
Sweden ⁹	4.2	45	2.3	20
Switzerland ¹⁰	--	8	--	25
United Kingdom ¹¹	63	<1	--	80
United States ¹²	260	8 to 10	--	30
West Germany ¹³	40	15	--	

1. A. Samarin, BMI Limited, Sydney, Australia.
2. Various ready-mixed concrete producers and Statistics Canada.
3. H. Isabelle, Lafarge Canada Inc., Montreal, Canada.
4. J. Scanlon, Master Builders, Cleveland, U.S.A.
5. T. Azuma, Kao Soap Co., Tokyo, Japan.
6. G. Reichert, SKW, Trostberg, West Germany.
7. Tan C.W., Singapore Institute of Standards and Research, Singapore.
8. P. Fildjestaal, Elkem, Kristiansand, Norway.
9. Sarish Chandra, Chalmers University of Technology, Göteborg, Sweden.
10. G. Reichert, SKW, Trostberg, West Germany.
11. R. Lavery, Cormix Limited, Cheshire, England.
12. Various ready-mixed concrete producers and suppliers of superplasticizers.
13. G. Reichert, SKW, Trostberg, West Germany.

14 Malhotra

TABLE 2--PHYSICAL REQUIREMENTS AS
SPECIFIED IN CSA CAN3-A266.6-M85

Property	Calculation	Nonflowing water-reduced concrete		Flowing concrete	
		SPN type	SPR type	SPN type	SPR type
Water content, maximum, per cent	$\frac{T}{R} \times 100$	88 ¹	88 ¹	NA	NA
Slump retention of test mix after 20 min	$\frac{T \text{ final}}{T \text{ initial}} \times 100$	Final slump of the test mix shall be at least 50% of initial slump.			
Initial set, minimum in hours: minutes	T - R	-1:20	+1:00	-1:20	+1:00
maximum in hours: minutes		+1:20	+3:00	+1:20	+3:00
Compressive strength, minimum, per cent	$\frac{T}{R} \times 100 \times 1.05$				
1 d		150	130	100	100
3 d		130	130	100	100
7 d		125	125	100	100
28 d		120	120	100	100
6 months ²		100	100	100	100
1 year ²		100	100	100	100
Length change		If R exceed 0.030% T/R shall not exceed 1.35. If R is not more than 0.030%, T - R shall not exceed 0.010%.			
Air-void spacing factor, ^{3,4} maximum, mm	$\frac{T}{R}$	0.23	0.23	0.23	0.23
Relative durability factor, ^{3,4}	$\frac{T}{R} \times 100 \times 1.10$	100	100	100	100

¹See Clause 8.2.2., which deals with the proportioning of the concrete mix.²Applicable only when required by the purchaser or when no previous test or acceptable service record is available.³At the purchaser's option, either the air-void spacing factor or the relative durability factor may be used to determine acceptability.⁴Applicable only when tested in air-entrained concrete.

Note: T = test mix; R = reference mix.

TABLE 3--PHYSICAL REQUIREMENTS AS SPECIFIED
IN ASTM C 494-86 AND C 1017-85^A

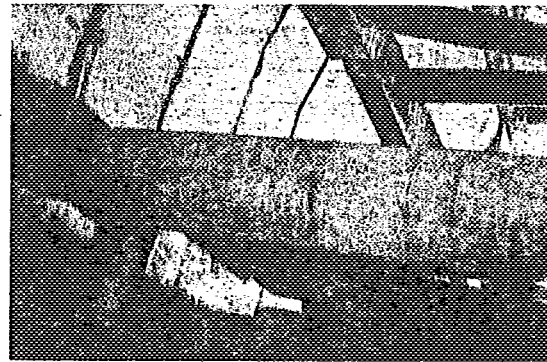
	C 494		C 1017	
	Type F, Water Reducing High Range	Type G, Water Reducing, High Range and Retarding	Type 1 Plasticizing	Type 2 Plasticizing and Retarding
Time of setting, allowable deviation from Reference, h				
Initial: at least	...	1 later	...	1 later
not more than	1 earlier nor 1 1/2 later	3 1/2 later	1 earlier nor 1 1/2 later	3 1/2 later
Final: at least	...	...	...	...
not more than	1 earlier nor 1 1/2 later	3 1/2 later	1 earlier nor 1 1/2 later	3 1/2 later
Increase in slump, in., min	...	...	3.5	3.5
Compressive strength, min., % of reference				
1 day	140	125	...	...
2 days	125	125	90	90
7 days	115	115	90	90
28 days	110	110	90	90
6 months	100	100	90	90
1 year	100	100	90	90
Flexural strength, min., % of reference				
3 days	110	110	90	90
7 days	100	100	90	90
28 days	100	100	90	90
Length change after 14 days drying, max.				
Shrinkage (alternative requirements): ^B				
% of reference	135	135	135	135
Increase over reference, in.	0.010	0.010	0.010	0.010
Relative durability factor, min. ^C	80	80	80	80

^A The values in the table include allowance for normal variation in the test results. The object of the 90% strength requirements is to require a level of performance comparable to that of the reference concrete.

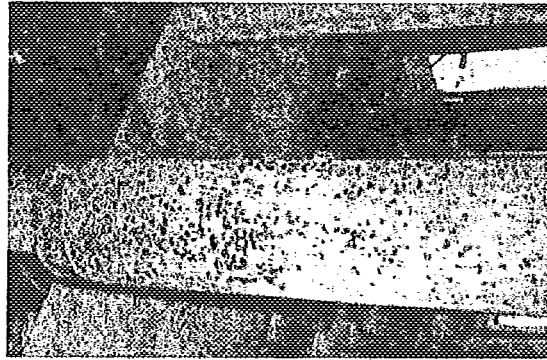
^B Alternative Requirements - Percent of reference limit applies when length change of reference is 0.030% or greater; increase over reference limit applies when length change of reference is less than 0.030%.

^C This requirement is applicable only when the admixture is to be used in air-entrained concrete which may be exposed to freezing and thawing while wet.

Note: For C 494, the compressive and flexural strength of the concrete containing the admixture under test at any test age shall not be less than 90% of that attained at any previous test age. The objective of this limit is to require that the compressive or flexural strength of the concrete containing the admixture under test shall not decrease with age.



Pile after repair-
uncollated fibers

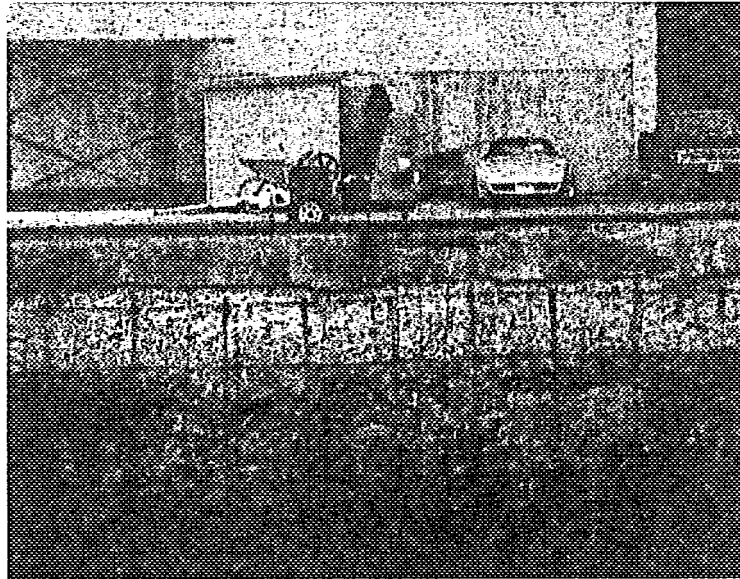


Pile after repair-
collated fibers

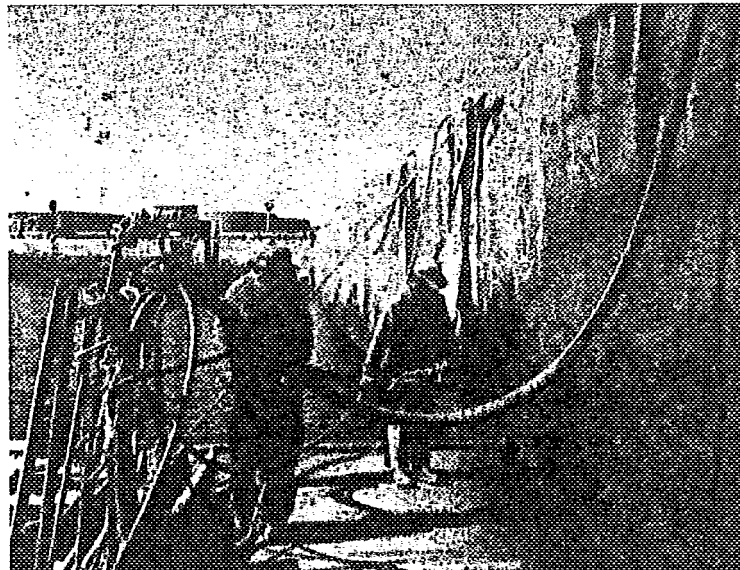


Distressed pile
before repair

Fig. 1--A view of reinforced concrete piles at Saint John's Harbour before and after repairs (Reference 15)



a) Prepared berth face, with anchor system installed, ready for shotcreting



b) View of shotcrete being applied to the berth face from the floating barge

Fig. 2--A view of the repairs being performed at Saint John's Harbour berth (Reference 16)

SP 119-2

Reuse of Returned Concrete by Hydration Control: Characterization of a New Concept

by F.D. Kinney

Synopsis: This paper discusses a chemical approach to dealing with returned concrete that has the potential of reducing the amount of waste in concrete production to a level unmatched by other methods. This approach allows use of concrete up to 72 hours after batching, and the reduction of wash-out slurry and reclaimer debris. This two part chemical system is comprised of a "stabilizer" that strongly retards the hydration of all clinker minerals, and a hydration initiator or "activator" added to stabilized concrete prior to its placement. Data presented on commercial portland cement and individual clinker minerals treated with this system show the effects of the stabilizer and initiator on the different clinker phases and were drawn from calorimetry, XRD, and SEM studies. Control of nucleation and nuclei growth are proposed as the mechanism by which the chemical system works. Data from field batched mixes demonstrate that the plastic and hardened properties of concrete made using this chemical system are no different than those of conventionally batched concrete.

Keywords: activators; chemical compounds; circulation; concretes; hydration; performance; ready-mixed concrete; retempering; stabilizers (agents)

20 Kinney

F.D. Kinney is a concrete petrographer and Principal Materials Researcher at Master Builders Inc., Cleveland Ohio. He has been involved with research on cements, pozzolans, and admixture systems for ten years.

INTRODUCTION

In 1987 an estimated 10 million cubic yards of concrete were returned to ready mix yards in the USA for disposal. An undetermined amount of water was used to wash out truck drums nightly, with about 600 pounds of mortar remaining inside each. Most of this concrete and wash-out water was disposed of at significant expense to the producers or the environment. To address the problem of disposing of this waste a novel approach has been developed which utilizes a two part chemical system that can reduce waste in a ready mix yard to a minimum. The first component or "Stabilizer" is composed of carboxylic acids and phosphorous containing organic acids and salts. The stabilizer is capable of retarding all clinker minerals and lowering the rate of calcium sulfate mineral solution. This is in contrast to conventional retarding admixtures which accelerate one fraction of cement while retarding others. This differential action on portland cement hydration by conventional retarders can, and often does, cause rapid stiffening of concrete when they are used at high enough doses to achieve the same degree of retardation experienced with the new "Stabilizer". The second part of this new system is a hydration accelerator or "Activator" that is added to stabilized concrete before placement.

There are many ways to take advantage of this system and a typical application is outlined here. Two cubic yards of concrete are returned at the end of a day. Enough water is added to the concrete to attain a 7 inch slump. Then 32 oz/CWT (20.8 mls/Kg) of the stabilizer are added, and the concrete is mixed thoroughly. The "stabilized truck" is then parked for the night. The next morning, the stabilized concrete will be agitated and 45 oz/CWT (29.3 mls/Kg) of the activator added. When agitation and activation of the concrete are completed, 8 cubic yards of fresh concrete, minus the weight of water added the day before to achieve the 7 inch slump, will be batched on top of the activated concrete.

It is already common practice that concrete returned before the end of a day is used if its workability is not too

low and a project is available. Such things as new parking lots in the ready mix yard or barrier blocks are favorite applications. If unusable, returned concrete goes to a land fill, a pile somewhere in the ready mix yard, or to a reclaimer. All three are expensive and unsightly. Wash-out water on the other hand has no alternative uses. It must be disposed of somehow. Most yards contain washout pits or settling ponds and many trucks are washed out on the job site or by the side of a convenient back road. While seemingly harmless to the industry, the US EPA takes a different view. It classifies wash-out water as a hazardous waste and regulates its disposal. In view of this regulation, no matter how a truck is cleaned out, legally the resulting material must be hauled to a land fill authorized to handle a hazardous waste. This is becoming more difficult to do as the number of licensed landfills in the USA has decreased 90% in the past few years.

Because so little has been published about the use of this chemical system, its unique properties and its effects on hydration and concrete performance, an investigation examining these two topics was conducted. Included in these studies were calorimetry, SEM, XRD, and tests on the physical performance of treated concrete.

EXPERIMENTAL

Calorimetry

The effects of this chemical system on the heat liberation of a type I portland cement and a blend of C₃A + gypsum were examined by calorimetry. The tests were conducted as follows. Four gram samples of powder were added to sample cells, sealed, and placed in a 70 F (21 C) constant temperature bath where they remained throughout the duration of the test. Mix water was drawn into 3 ml syringes and where appropriate a diluted solution of stabilizer was added to allow for the small volume doses required by 4 gram samples. These syringes were then inserted into septa in the sample cell. When the cells had equilibrated with the water bath they were injected with either water or water plus stabilizer. Cell No.1 was always the reference and had only one injection of mix water. Cell No.2 had an injection of diluted stabilizer and was at the same W:C as Cell No.1. Cells No.3 and 4 had a total of three injections. One each of mix water, stabilizer, and activator.

Portland Cement—This test was run to determine the effects of stabilizer addition time on the activation of portland cement.

22 Kinney

Procedure—A 0.5 W:C was used for the initial mix water. Sample No.2 also contained an equivalent stabilizer dose of 35 oz/100 lbs of cement (CWT), (22.8 mls/Kg). After initial mix water injection a concentrated dose equal to 35 oz/CWT (22.8 mls/Kg) of stabilizer was added to the syringes in Cells No.3 and 4 and left to equilibrate with the bath. At 2 hours after initial injection and during the induction period, Cell No. 3 was injected with stabilizer and remixed. At 6 hours after injection and during the secondary heat rise, Cell No.4 was injected with the same dose of stabilizer. The samples were then left for 18 hours. At this point the syringes in Cells No.3 and 4 were loaded with an equivalent activator dose of 90 oz/100 CWT (58.5mls/Kg) and at 24 hours these cells were injected for the third time. The cells were then left to run over a weekend.

Results—The sample in Cell No.2 that was stabilized with initial mix water behaved as any excessively retarded cement would. No noticeable change in the rate of heat liberation was recorded in the first 24 hours except for a small increase ending 2 hours after the initial injection. When activated at 24 hours a significant amount of activity was recorded in a heat peak possessing the shape of an initial heat of solution and hydration that characteristically appears just after initial injection. A third heat peak followed with a maximum rate of heat liberation recorded at 29 hours or 5 hours after activation. This was compared to the the secondary heat peak in the reference sample in Cell No.1 having a maximum rate of heat liberation at 10 hours after initial mixing. The obvious difference in this comparison was the total area under the curves. The sample in Cell No.3 was stabilized during the induction period and data from this cell illustrates the importance of addition time. A delay of 2 hours after initial injection and during the induction period of the cement prevents any significant hydration from occurring. Although a small rate increase did occur over an 8 hour period similar to the one in cell No.2 that occurred at 1 hour. A third rate increase at 17 hours appears to coincide with a depletion of gypsum. The remainder of data from this cell even after activation shows the cement to be very slowly reactive.

The sample in Cell No.4 was stabilized at 6 hours after the initial injection of mix water. The data from this cell demonstrates the remarkable ability of the stabilizer to halt hydration and the ability of the activator added at 24 hours to initiate further hydration. The shape of the major secondary rate curve suggested a depletion of available sulfate and renewed hydration of the aluminate phases, but the area under the curve is not much reduced from the reference. Physical strength data from concrete treated in a similar manner showed

no signs of retrogressive strength. This suggested that there were no ill effects if aluminate hydration was renewed at this point.

Tricalcium Aluminate and Gypsum--Samples for this test were prepared from 4 gms of laboratory produced C_3A having a Blaine surface area of 3600 and 7.82 gms of reagent grade gypsum. Only two cells were used because during preliminary trials it was learned that delayed stabilization of the mixture was impossible mainly due to rapid stiffening soon after water injection. Activation was unnecessary because most reactions were completed in less than two hours.

Procedure--The test was set up and run as follows. Both Cell No.1 and 2 were loaded with a 4 gm sample of powder. 2.4 mls of water were placed in the syringe of Cell No.1 and a diluted solution of the stabilizer equivalent to a 35 oz/CWT (22.8 mls/Kg) dose was placed in the syringe of Cell No.2. After the cells had equilibrated with the water bath both cells were injected and mixed.

Results--The data from both of the cells in the calorimeter tests on C_3A , Figure 2, illustrates two things. The unhampered reaction was very rapid and while the stabilizer retarded the formation of ettringite, it did not have the same profound effect that it has on the silicate fraction of portland cement. The same amount of C_3A retardation was seen in both the calorimeter tests on portland cement and C_3A . Cell No.2 from Figures 1 and 2 were both stabilized with the initial mix water injections. They show an aluminate rate peak at about 1.5 hours. The other data from the runs on portland cement did not exhibit this peak suggesting a change in action of the stabilizer when the cement was allowed to develop normal hydrates prior to stabilization. Finally, it was apparent that the area under the rate peak was significantly larger in Cell No.2 data. This was most probably due to the increased efficiency of hydration afforded by a dispersing effect the stabilizer has.

Scanning electron microscopy, (SEM)

Scanning electron microscope examinations were made on samples of normal, stabilized, and stabilized then activated portland cement pastes. The purpose of the work was to compare the way in which surficial hydrates formed on clinker minerals before, during, and after stabilization and determine if changes in reaction products could explain the performance of the admixture system.

24 Kinney

Procedures—Samples studied using the scanning electron microscope (SEM) were first washed with acetone and vacuum dried at room temperature. After drying they were mounted on aluminum buttons coated with 200 angstroms of gold and palladium and stored in a desiccator until examination. The SEM was equipped with an energy dispersive x-ray spectrometer which provided identification of particles that could not be identified by morphology alone.

Observations—For comparison, Figure 3 illustrates the appearance of one day old hydrates formed from the water-only hydration of the type one cement used in this study. Figure 3a illustrates a fairly open structure of silicate hydration products common of young paste. The large bladed crystals are CH. Figure 3b is a close up of a large alite crystal. The surface of alite once covered with CSH has been exposed. It appears to be pitted with minor amounts of hydrate still adhering there. A close up of the CSH, Figure 3c, shows the hydrates to be a combination of sheets and needles. In contrast to the surface of alite hydrated only with water, stabilized alite shows no pitting and few products of hydration after one day, Figure 4a. The surface has only isolated spots with hydration products, and these were determined by EDS to be aluminates hydrates that appear to have precipitated out of solution. Higher magnifications of the alite surfaces detail the nature of the aluminates hydrates that resemble bullock ettringite crystals, Figure 4b and 4c. After activation, Figure 5, the initial hydrates were determined by morphology and EDS to be predominantly aluminates, although some CH and possibly CSH can be seen. One day after activation the paste took on the appearance of normal but somewhat denser silicate hydrates, Figure 6.

SEM examination of the C_3A and gypsum reaction confirmed the calorimeter study results. While retarded by the stabilizer, the hydration of C_3A with gypsum progressed rapidly. Photomicrographs also indicated that the stabilizer not only retarded the reaction, but altered the texture of the hydrates that were formed. Figure 7 shows the appearance of a C_3A + gypsum paste hydrated with water. At 1500 X only a dense mass was discernible and took up the whole field of view. At 4000 X the mass is seen to be made up of 2-3 micron ettringite crystals. This same sample, stabilized after ten minutes of reaction had a totally different appearance when magnified 1500 times, Figure 8. Although the crystals were approximately the same size, the structure was more open.

X-ray diffraction, (XRD)

One way the value of a hydration inhibitor can be measured is by its ability to lengthen the time concrete is workable. Conventional retarders are very effectively used for this purpose but are limited to relatively small doses because of their tendency to accelerate some reactions while retarding others. Normally, retarders slow alite hydration and delay CH and CSH nucleation and growth for a few hours. C_3A + gypsum reactions are slowed but continue and produce essentially their normal hydrates within minutes. The stabilizer on the other hand halts all portland cement hydration in mid reaction, as demonstrated by the portland cement calorimeter study above. The calorimetry study also shows that the addition of an activator causes a significant increase in the rate of some reaction. A question remains however; what reactions are initially accelerated after activation? The SEM examination suggests that while cement is stabilized, aluminates continued to precipitate out of solution. Even after activation, the surfaces of alite are coated predominantly with ettringite-like crystals. Only after activation and one day of hydration are normal appearing silicate hydrates present. One way of answering this question is to measure the rate of alite hydration by XRD. If significant hydration occurs, CSH will be the major product. If not, early aluminate precipitates are the most probable hydration product.

Procedures—Samples for quantitative XRD (QXRD) were prepared from the same lot of type I portland cement used in the calorimeter study. Three conditions were examined; unstabilized, stabilized, and stabilized with subsequent activation at 24 hours past mixing. All samples contained 50 gms of cement and 20 gms of either water or a stabilizer solution diluted to deliver an equivalent dose of 35 oz/CWT (22.8 mls/Kg). The samples that were later activated were treated with 2.42 gms of activator which is equivalent to a 90 oz/ CWT dose (58.5 mls/Kg).

After mixing, samples were sealed in polypropylene containers until their hydration was stopped by acetone. Samples that were still fluid were simply shaken and filtered. Hardened samples were crushed in acetone in a mortar and then filtered. These samples were passed through a 104 micron sieve and then x-rayed. To improve resolution, all samples were milled in a Spex Mixer Mill for 10 minutes with 1,1,2, trichlorethane. These samples were also x-rayed. This double procedure was carried out to monitor any changes in the sample caused by preparation. All measurements were compared to an external quartz standard. Alite hydration was monitored by determination of the peak areas of the 51.7 degree 2 theta

26 Kinney

reflection. In addition, CH was monitored by measuring the 18 degree 2 theta reflection. Because CH is not always crystalline in portland cement and cannot always be detected by XRD only the peak heights were recorded as an estimation.

Results---Data in Figure 9 indicated that as with retarding admixtures, the hydration rate of alite treated with stabilizer was significantly reduced in the first 3 days. By 7 days the total alite remaining is practically the same whether the cement was stabilized, activated or contained no stabilizer. The sample that was stabilized at 6 hours and activated at 24 hours did show slightly more alite consumed at 3 days, but from 3 to 7 days there was no apparent change in the rates. This suggests the influence of activation was short lived. Measurement of CH produced slightly different results (Figure 10). While the increase in CH from the hydration of alite was normal for the sample without treatment addition, the stabilized samples showed very little detectable CH even out to 7 days. The activated sample showed slightly more CH, but both treated samples produced far less detectable CH than the amount of hydrated alite would normally have produced.

Concrete performance

There are three ways this system has been used. To reduce the amount of wash-out water, to hold concrete for use on the same day it was batched, or to hold concrete overnight. All three practices have been shown to produce quality concrete when used correctly. To insure success of these applications there are several factors that should be considered. These are concrete temperature, presence of mineral admixtures, cement content, and cement type. New considerations include knowing the age, volume, and the presence conventional admixtures in the returned concrete. Below are three examples of successful field use of the chemical system.

Overnight stabilization of washout water---At the end of a day, 60 gals (227 liters) of water and 1 qt. (0.9 liters) of stabilizer were added to a truck that had contained 517 lb cement factor concrete. The drum was turned for 5 minutes to agitate the contents and then the truck was parked for the night. The next morning, 9 yards of concrete with the same mix design as used the day before was batched into the truck. A correction of the 60 gals (227 liters) was made for water already in the truck. This was mixed and sampled for Proctor ROH and compressive strength. A second truck was also batched immediately after the first as a reference. It contained the same mix as the first but had no washout water in it.

Concrete from the reference truck set in 5.1 hours while the truck with the washout water set in 5.2 hours. The 7 and 28 day compressive strengths of the reference concrete were 3690 psi (22 MPa) and 6400 psi (44 MPa) while the concrete containing the washout water had compressive strengths of 3840 psi (26 MPa) and 6620 psi (45 MPa).

Same day stabilization of concrete--Two cubic yards of concrete were returned two hours and twenty minutes after batching. They were immediately stabilized with a stabilizer dose of 10 oz/CWT (6.5 mls/Kg). Once the stabilization was complete five fresh yards of concrete with the same mix design were batched on top and sent out. A second 7 yards containing no admixtures were batched as a reference. Both concrete and ambient temperature were 89 F (32 C).

The reference concrete set in 3.7 hours while the concrete containing the stabilized load set in 3.8 hours. The 7 and 28 compressive strengths for the reference concrete were 2485 psi (17 MPa) and 3920 psi (27 MPa) while the concrete with the stabilized had compressive strengths of 3115 psi (21 MPa) and 4620 psi (32 MPa).

Overnight stabilization--One cubic yard of concrete at a 6 inch slump and containing 517 lbs of cement was returned from the field two hours after batching. A stabilizer dose equal to 35 oz/CWT (22.8 mls/Kg) was added to the load and thoroughly mixed. The next morning, 14.5 hours later, an activator dose equal to 40 oz/CWT (26 mls/Kg) was added to the load. To this concrete an additional 2 cubic yards of fresh concrete were added. The total 3 yards was then mixed thoroughly and sampled for Proctor ROH and strength measurements. Two additional yards of identical fresh concrete were also mixed and used as a reference. The reference concrete set in 5.5 hours while the concrete containing the stabilized load set in 4.5 hours. The 7 and 28 day strengths for the reference concrete were 2710 psi (19 MPa) and 3710 psi (26 MPa) while the test concrete had compressive strengths of 4120 psi (28 MPa) and 5260 psi (36 MPa).

DISCUSSION

Controlling the rate of portland cement hydration with conventional accelerators and retarders is common practice. The ability to almost stop hydration for up to 72 hours and then activate that concrete so that is possible to use it to produce a normal setting, quality concrete is novel. The mechanism by which this system accomplishes this is explained most completely

28 Kinney

by how the stabilizer effects the hydration of alite and C_3A , and the subsequent formation and growth of both calcium silicate and aluminate hydrates. The process can be thought of as forcing a metastable equilibrium on the system until such time as renewed reaction is desired or until the effect wears off, and the cement spontaneously begins to hydrate.

Any mechanism proposed to describe the hydration of portland cement must account for the behavior of admixtures or it cannot be considered valid. It is believed that hydrate nucleation control best explains the behavior of most if not all admixture-cement interactions. Recently, Taylor (1) summarized the various hydration mechanisms proposed to explain the induction period of portland cement. This period of little reaction in the hydration of portland cement is the period that set controlling admixtures either extend or shorten to increase the versatility of concrete. Grutzeck and Ramachandran (2) believe at the beginning of this period alite forms a primary hydrate in metastable equilibrium that persists until it reacts with itself, the under lying alite, and the pore solutions to form a secondary hydrate. As the secondary hydrate forms, CH precipitates out of solution and initial set begins. Jennings (3), characterizes two distinct metastable CSH hydrates. One low in calcium that may represent a first hydrate close to a hydrating grain, and a one relatively higher in in calcium believed to be a second hydrate. Taylor (1) arrived at the conclusion that delayed nucleation and growth of CSH was the most probable explanation for control of the induction period. Thomas and Birchall (4,5) concluded that conventional retarders act by a poisoning of nuclei preventing the growth of CSH. Young (6) in an earlier paper used a similar argument for the poisoning of CH nucleation and growth.

The data presented above which best support the belief that this chemical system controls the nucleation process of hydrates in a more comprehensive manner than conventional retarders are the calorimetry data (Figures 1 & 2) and SEM photomicrographs of the surfaces of stabilized and activated alites in portland cement (Figures 4 thru 6). Examining the calorimeter data (Figure 1, Cell 2) it can be seen that the stabilizer added along with the mix water behaves as a CSH and CH nucleation inhibitor in that it is essential for these two species to nucleate, grow, and precipitate before set can occur. The calorimeter monitors the formation of these species by an increase in the evolution of heat. The time of this increase in Cell 2 was significantly delayed compared to the reference concrete in Cell 1 and really only began after the sample was activated. The heat generated was a direct

consequence of alite in the portland cement reacting with the water and it was this reaction that the stabilizer worked most effectively upon.

The C_3A in portland cement was also moderately effected by the stabilizer. This was demonstrated by a small heat rise at about 1.5 hours in Cell 2, Figure 1 and in Cell 2, Figure 2. That C_3A reacted relatively fast when stabilized compared to alite points out an important property of the stabilizer. The stabilizer is a surface active compound designed to prevent surface nucleation of calcium rich hydrates. When nuclei have already formed the stabilizer retards their growth and alters the external morphology of subsequently formed hydrates. The stabilizer's ability to stabilize primary CSH hydrates, and its moderate slowing of C_3A hydration suggest that in portland cement the stabilizer prevents epitactic growth (growth on surfaces) of primary CSH on C_3S while only slightly slowing C_3A hydrates from precipitating out of solution.

The data from Cell 3, Figure 1 further illustrate the surface active nature of the stabilizer. In this cell, the cement was stabilized during the induction period, when primary CSH coated alite and ettringite coated C_3A . Addition of the stabilizer at this point prevented not only CSH conversion to secondary hydrate, ending the induction period, but it prevented the layer of ettringite coating C_3A from reacting with the pore solution. The effectiveness of the stabilizer as a surface active agent to force a metastable equilibrium on the system is very apparent because even after activation the cement in Cell 3 was very slow to react.

Apparently, when the stabilizer was added after the end of the induction period, its ability to halt the precipitation of CH and the renewed reaction of alite at the end of the induction period, was less than when it was added during the induction period. Data from Figure 1, Cell 4 show that forcing a metaequilibrium state on the system at this point resulted in a much quicker and larger degree of reaction after activation.

Although we can not yet directly represent the action of this chemical system on hydrate nucleation, there are data that indirectly illustrate these effects. The alteration of the ettringite morphology on alite in Figures 4 & 5, and the more open texture of ettringite on C_3A in Figures 7 & 8, strongly suggest that the stabilizer effected how these hydrates formed. The effects on the reduction of CH crystal size, illustrated in Figures 4 thru 6, were supported by an inability to detect the expected amount of CH by XRD, Figure 10, in samples that had hydrated for 7 days.

30 Kinney

It is possible that the small CH crystal size may be a contributing factor to some of the improved engineering properties recorded from field and lab made concretes. Many of these engineering properties are derived from the amount and nature of the alite hydration reaction products. More hydrates translate to more strength. Data from Figure 9, reveal that whether the cement was stabilized and subsequently activated, or stabilized and left alone, the amount of alite that hydrated before 7 days is less than untreated cement. At 7 days of age, samples attain about equal degrees of hydration no matter how they were treated. However, the strength data collected from field and lab samples of concrete and reported above indicates that the treated concretes have slightly higher strengths even though they have the same amount of hydration than an untreated concrete. The nature of the CH has already been discussed to this regard but the nature of the CSH may also play a part. If the pastes in the photomicrograph, Figure 3, are compared to the pastes in Figure 6, a significant density increase is apparent. This increase may have had a positive effect on the paste's strength.

SUMMARY

1. A novel chemical system useful for controlling portland cement hydration is characterized. The system can be used to reclaim wash out water or slow hydration until such time as set is desired, for up to 72 hours.
2. The stabilizing part of the system predominantly effects C_3S hydration but can also delay the initial C_3A reaction with water and sulfate for up to 1.5 hours if the stabilizer is added with mix water, or it can slow the conversion of ettringite to monosulfate when it is added during the induction period.
3. It appears that the system slows CSH nuclei formation when added with mix water, and it slows CSH and CH nuclei growth when added during or after the induction period. The ability to slow hydration depends upon how developed these nuclei are, and possibly how many have developed.
4. An ability to effect nucleation and crystal growth causes finer CH and denser silicate hydrates to form. This effect appears to benefit physical paste properties.

REFERENCES CITED

1. Taylor, H.F.W., (1986) "Chemistry of Cement Hydration", 8th International Congress on the Chemistry of Cement, Vol.1, p.82-110.
2. Grutzeck, M.W., and Ramachandran, A.R., (1987) "An integration of tricalcium silicate hydration models in light of recent data", Cem. Concr. Res. 17 (2) p.164-170.
3. Jennings, H.M., (1986) "Aqueous Solubility relationships for two types of calcium silicate hydrate", J. Am. Ceram. Soc., 69 (8) p.614-618.
4. Thomas, N.L., and Birchall, J.D., (1983) "The retarding effect of sugars on cement hydration", Cem. Concr. Res. 13 (6) p.830-842.
5. Birchall, J.D., and Thomas, N.L., (1984) "The mechanism of retardation of setting of OPC by sugars", Proc. Brit. Ceram. Soc. (35) p.305-315.
6. Young, J.F., (1972) "A review of the mechanisms of set-retardation in portland cement pastes containing organic admixtures", Cem. Concr. Res. 2 (4) p.415-433.

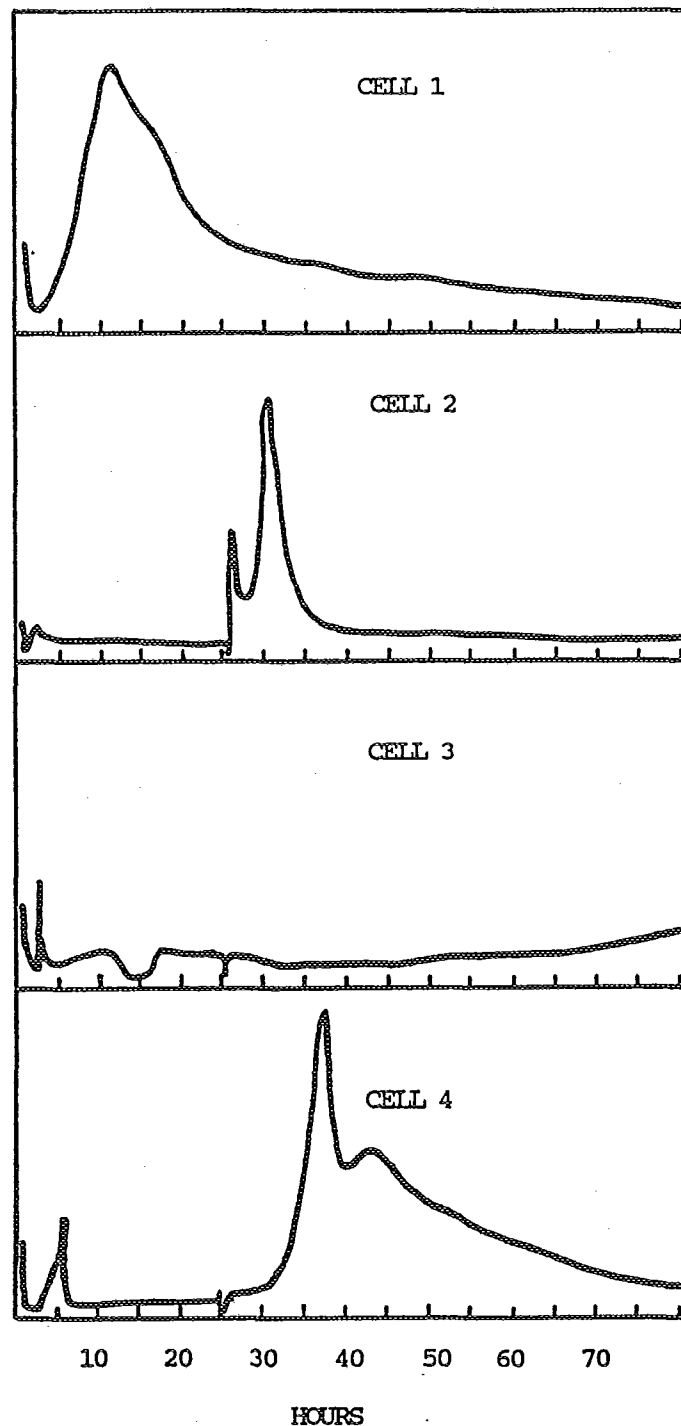


Fig. 1--Calorimetry of type I portland cement --Cell 1 is a reference, Cell 2 had stabilizer added with the mix water, Cell 3 was stabilized at two hours, and Cell 4 was stabilized at 6 hours -- Cells 2, 3, and 4 were activated at 24 hours

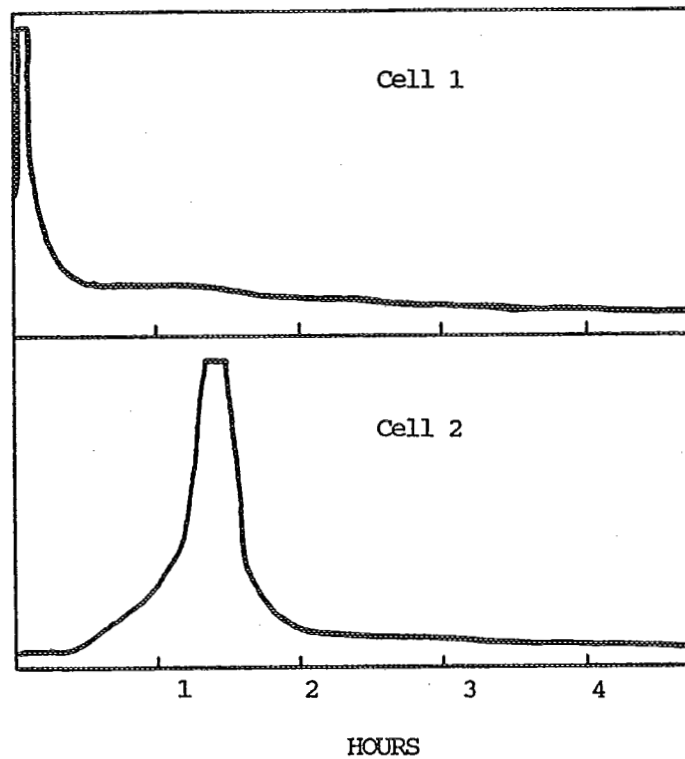


Fig. 2---Calorimeter data for laboratory produced C_3A + gypsum --- Cell 1 was hydrated with water, Cell 2 was hydrated with a diluted stabilizer solution

34 Kinney

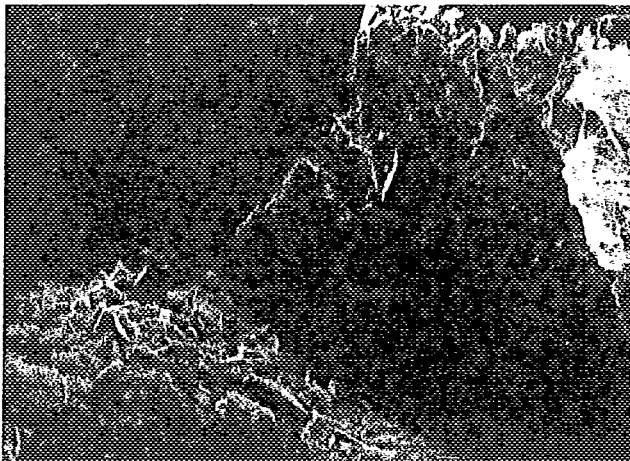
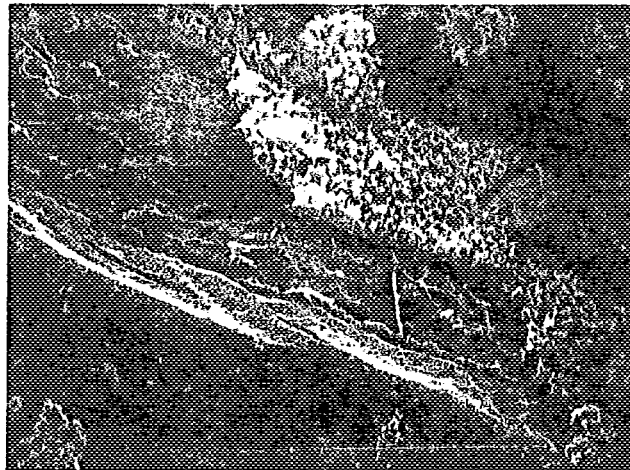
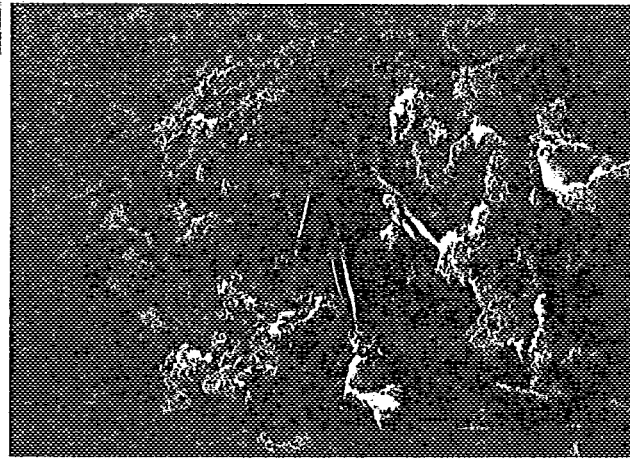


Fig. 3--SEM photomicrographs of one day old portland cement paste hydrated with water -- magnifications: 3a = 1700X, 3b = 4650X, 3c = 11,800X

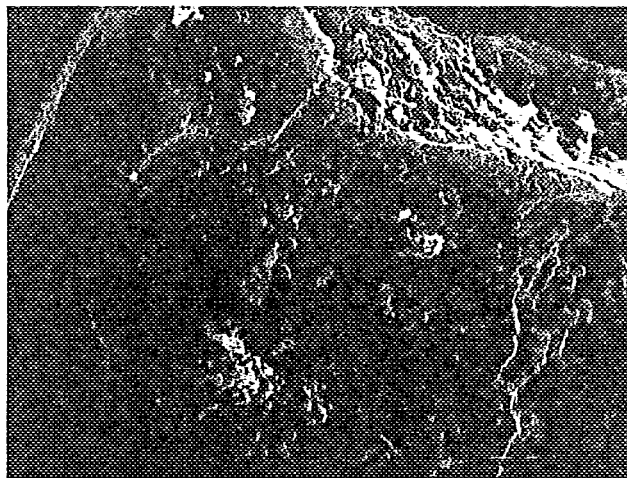
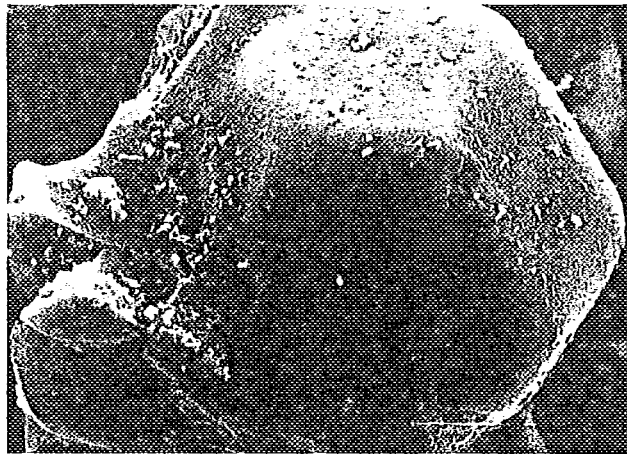


Fig. 4--SEM photomicrographs of one day old cement paste hydrated with a dilute solution of stabilizer --- magnifications: 4a = 1700X, 4b = 3500X, 4c = 16,100X

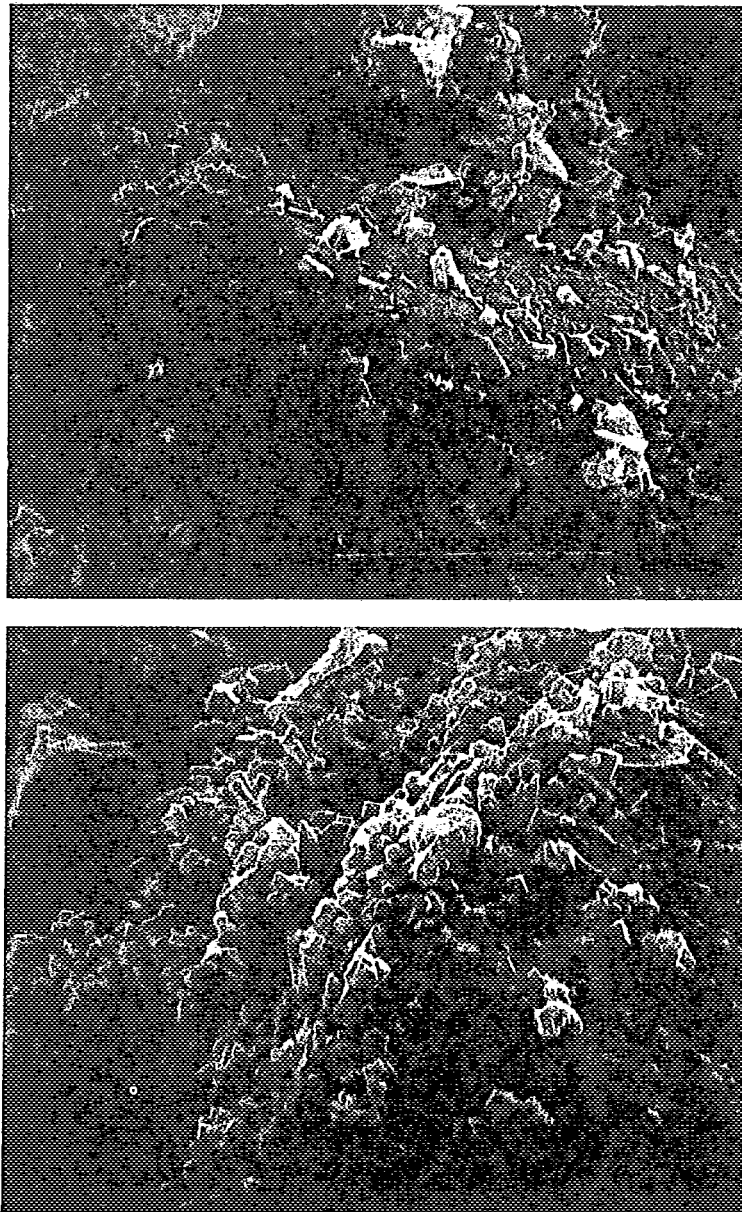


Fig. 5--SEM photomicrographs of portland cement hydrated for one day with a dilute stabilizer solution and then activated -- magnifications: 5a = 3820X, 5b = 6100X

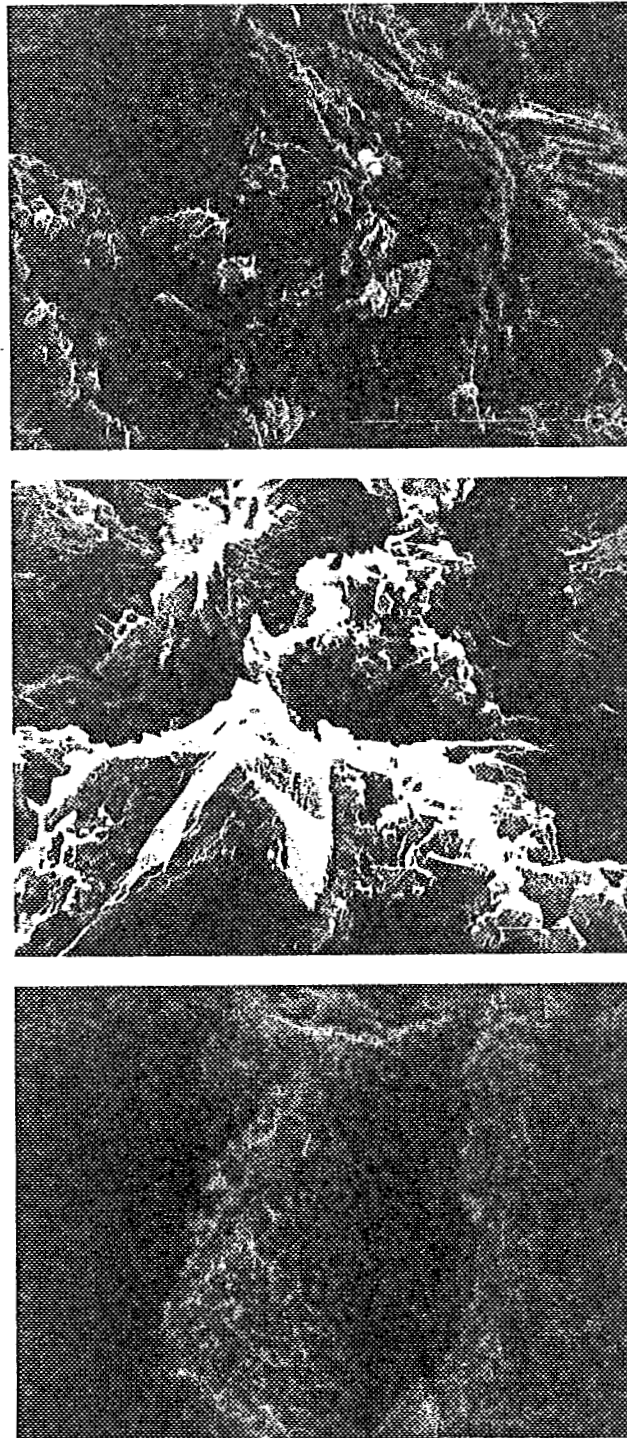


Fig. 6--SEM photomicrographs of stabilized portland cement paste 24 hours after activation -- magnifications:
6a = 3000X, 6b = 6100X, 6c = 16,100X

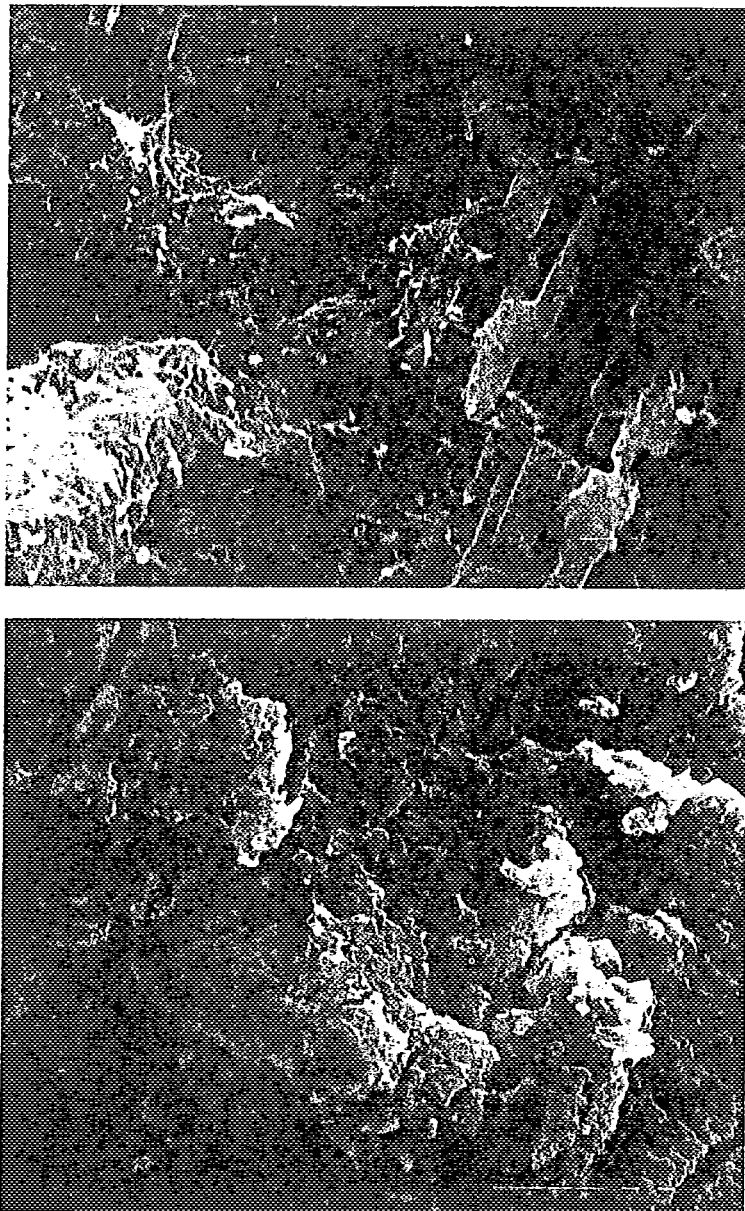


Fig. 7---SEM photomicrographs of C_3A + gypsum, hydrated with water -- magnifications: 7a = 1500X, 7b = 4100X

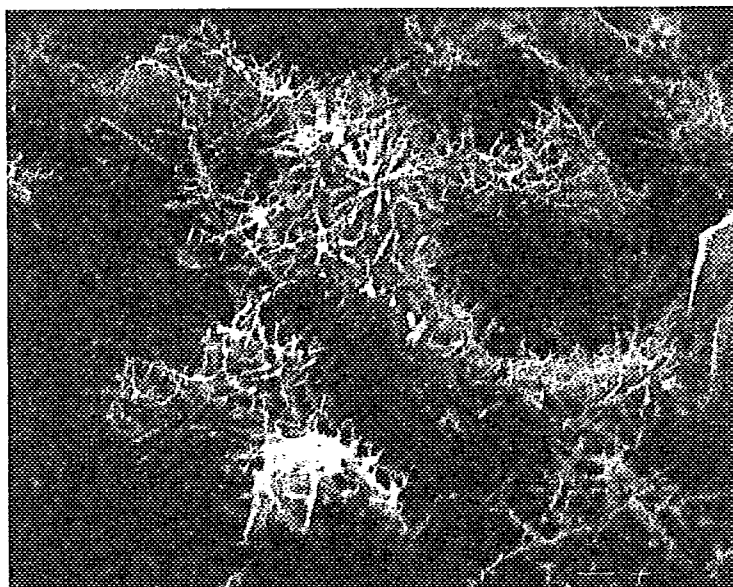
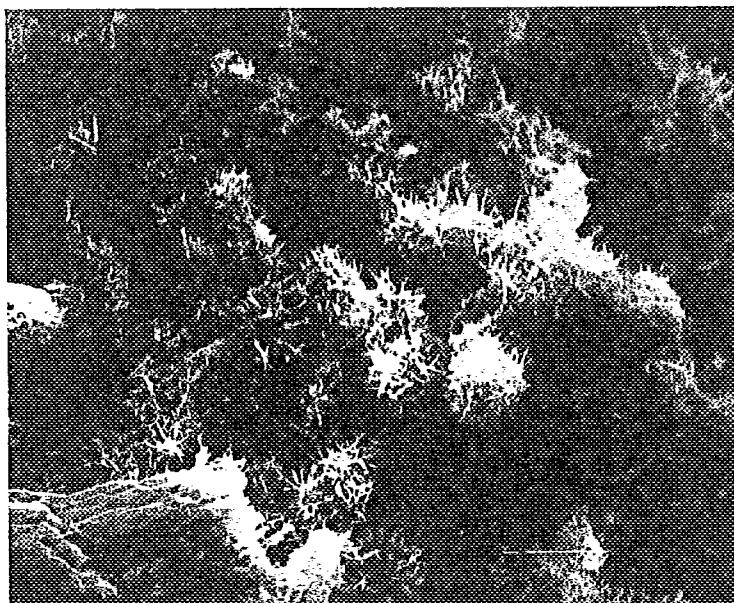


Fig. 8--SEM photomicrographs of C_3A + gypsum stabilized with a dilute stabilizer solution --
magnifications: 8a = 1500X, 8b = 4500X

ALITE HYDRATION RATE

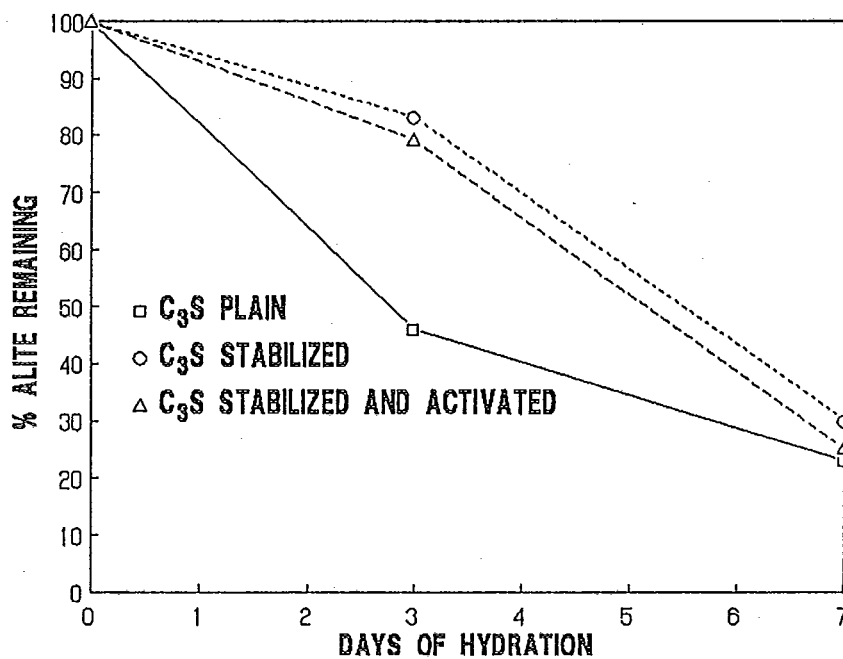


Fig. 9---Graph of the alite rate of hydration as measured by QXRD

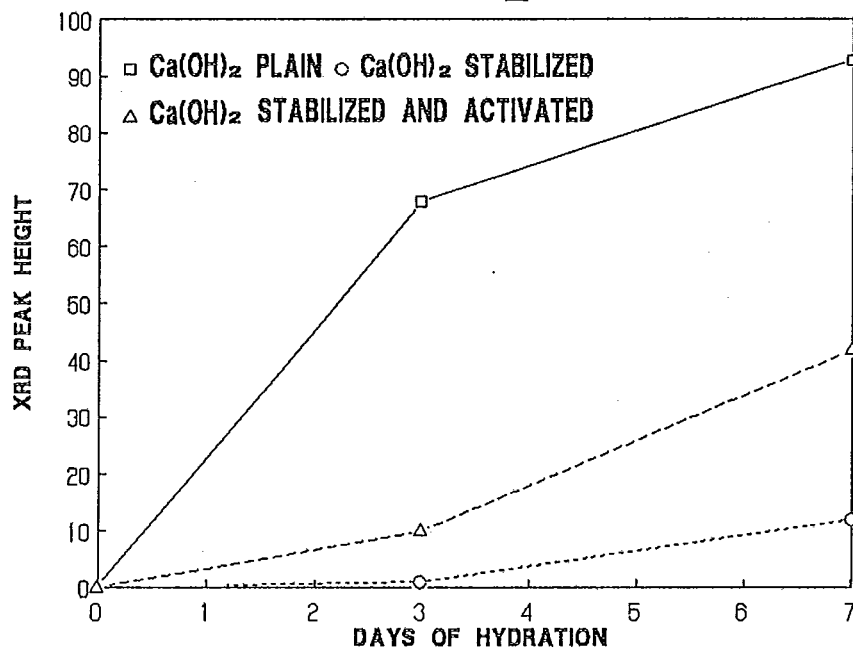
RATE OF Ca(OH)_2 PRODUCTION

Fig. 10---Estimated rate of CH production as measured by XRD

SP 119-3

Case Histories—The Use of Superplasticizers in Two Extremes of Concrete Placement Difficulties

by A.J. Hulshizer, J.J. Ucciferro, and G.E. Gray

Synopsis:

This paper describes the expanded achievements possible in concrete placements with the aid of superplasticizers and identifies the importance of pre-placement testing and planning to determine structural performance and placing characteristics and limitations. Different combinations of cement types and brands, superplasticizers and other additives can produce significantly different results and apart from proven experience, the superplasticized mix planned as a panacea could produce unsuspected surprises and problems.

The two concrete placement extremes discussed in this paper involved 98,000 m³ of large diameter tunnel lining and 104 m³ of a complexly reinforced, miniaturized nuclear reactor containment test model. The use of superplasticizers in these divergent concrete structures was considered a necessary factor in being able to achieve reasonable concrete placements, commensurate with the high quality in-place concrete needed to have the structures meet their performance requirements.

Keywords: admixtures; concretes; performance; placing; plasticizers; tests

42 Hulshizer, Ucciferro, and Gray

Allen J. Hulshizer - Employed by United Engineers & Constructors, Inc. (UE&C) since 1961, Supervising Engineer for the Seabrook Nuclear Station.

Joseph J. Ucciferro - Project Manager for UE&C. Formerly Assistant Chief Structural Engineer.

George E. Gray - Manager Field Projects for UE&C. Formerly Manager International Construction Operations.

GENERAL INTRODUCTION

Two tunnels, excavated to produce inverted siphons, 79 m below land and sea, 6.7 m in diameter and 10.2 km in total length, required long transportation and handling time to place the concrete lining, but conversely needed 14 hour strip time to facilitate the 5 day per week continuous concrete placement method employed. Three brands of superplasticizers were evaluated to obtain the performance needed. An in-tunnel test program was utilized to confirm handling and strength gain performance prior to initiating production placing of the lining of the tunnels. The information and confidence established in the tunnel program led to the eventual use of superplasticizer throughout the project's safety-related structures, which was the first known use of its kind in the U.S.A. nuclear industry.

A scaled down nuclear containment building, 6.7 m in diameter, utilized 2 to 3 m³ placements in constructing the 25 cm thick concrete shell under difficult access and consolidation conditions. These placements required flowable concrete in the 20 to 25 cm slump range which could be pumped through a 50 mm diameter hose line. The remote location of the model construction site added further difficulties to securing the needed concrete placement qualities while still meeting the design criteria. A combination of trial mixes and dry runs utilizing a mock-up of the actual shell placement was successful in developing a superplasticized mix and re-dose criteria that enabled the model to be constructed as required.

TUNNEL PROJECT

Introduction

The concrete tunnel lining work was for the Seabrook Station, a nuclear powered electric generating station, located at Seabrook, New Hampshire, about 65 km north of Boston, Massachusetts, USA. The use of the Atlantic Ocean as a water supply enabled the use of a once-through cooling system, involving two independent tunnels to obtain cooling water through one, and to discharge the heated water through the other. A diagrammatic sketch of the tunnel system is shown in Fig. 1. A scaled profile and typical tunnel section is shown in Fig. 2.

Geological conditions necessitated a deep tunnel to obtain sound rock for excavation and tunnel roof support. Marine environmental considerations dictated the location of the intake and discharge ports over 1.6 km off the shore line. Vertical shafts were used on each end of the tunnels to connect the offshore water ports and the plant cooling water system, creating a deep inverted siphon 79 m below the surface on the land end and 46 m below the ocean surface on the offshore end. Information relative to the sinking of the land and ocean shafts, tunnel excavation and geological investigation can be found elsewhere (1-4).

Although much of the tunnel was located in sound, massive rock, sufficient lengths of less stable rock demanded a concrete lining to insure continued service of the tunnels. To assure risk-free operation and for practical construction reasons, the concrete lining was placed along the entire length of both tunnels. The lining has a nominal construction thickness of 46 cm with a minimum design thickness of 38 cm and a final inside tunnel diameter of 5.8 m. The concrete lining is reinforced on both faces to additionally resist forces associated with temperature transients created by the cooling water thermal cycling. The cooling water system is indispensable to the operation of the \$5.5 billion plant and, therefore, it is imperative that it perform maintenance free for the 40 year plant design life. The durable quality of the tunnel concrete lining is a vital element in achieving the uninterrupted supply of plant cooling water.

Superplasticizer Introduction and Consideration

Considerable efforts were initially made to develop a 28 MPa, 28 day cylinder strength concrete mix with the specified cement (Table 1) which would produce 12 to 18 hour strengths in the range of 7 MPa and still be placeable with a nominal 100 mm slump up to 3 hours after batching. A number of admixtures were tried at the project's test laboratory and at manufacturers' testing facilities. None of the mixes tested would produce both early strength and the 3 hour workable duration.

Superplasticizers had, as of then, been untried at Seabrook but their basic claims to improve both strength and workability were of obvious interest.

While superplasticizers's concrete strength and workability claims were of interest, the reported short effective life in the range of one-half to one hour were a major concern due to the need for much longer handling times. As part of the evaluation into the use of superplasticizers, various schemes were investigated to have the superplasticizer introduced into the concrete mix along the route or near the placement area to accommodate the reported short duration superplasticizing

44 Hulshizer, Ucciferro, and Gray

effect. Due to the logistics involved with transferring the concrete to the tunnel level and out to the placement zone, feasible arrangements for this introduction could not be made. The close confines of the tunnel diameter and the existing concrete agitation tunnel transfer cars, further restricted the ability to add and mix a superplasticizer out in the tunnel proper. The final conclusion was that a superplasticizer must be added to the concrete either in the original mixing at the on-site batch plant (the most desirable introduction) or at the surface into the truck mixers by either truck dispensers or a large tank set-up with a metering station. At this point of planning, the ability to practically implement the use of a superplasticizer in the tunnel concrete mix was doubtful even if the technical requirements of the mix were achieved and for a short time, consideration for its use was abandoned.

Superplasticized Concrete Mix Qualification Criteria

Because of the continued need, the purported promise of improved concrete placing characteristics spurred further testing to qualify superplasticized concrete for other work in the nuclear station structures.

The complete Seabrook test program covered over nine months of work and involved more than 380 m³ of placed and laboratory tested concrete integrating the efforts of construction and engineering personnel. The object of the test program was not only to assure compliance with the standard technical requirements but to also evaluate field associated parameters which ultimately affect construction performance and cost. Test samples were, therefore, also taken from large test placements to supplement laboratory work with relevant field data monitored to fully evaluate superplasticized concrete for the Seabrook project.

The basic technical requirements for concrete admixtures are given in ASTM C494, "Chemical Admixtures for Concrete" (Ref. 8). This standard imposes a series of typical concrete evaluators (slump, air content, setting time, strength and freeze-thaw resistance) to examine the effects of admixtures on fresh and hardened concrete. Because of the reported effect of superplasticizers to reduce the final air content of concrete (5 and 6), particular attention was given to ASTM C666, "Test for Resistance of Concrete to Rapid Freezing and Thawing".

Tests were also carried out to confirm the paintability of superplasticized concrete. Although initially conducted to qualify concrete mixes for nuclear safety-related structures, the successful results did prove to be of use to confirm the suitability of coatings application in certain remedial tunnel lining repairs.