National Library of Canada

Acquisitions and Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale du Canada

Direction des acquisitions et des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

Canada

CONVERSION PREVENTION IN HIGH ALUMINA CEMENT PRODUCTS

by

JIAN DING

Department of Civil Engineering

A thesis submitted in conformity with the requirements
for the Degree of Master of Applied Science in the
University of Ottawa

The M.A.Sc. program in Civil Engineering is a joint program with Carleton Univeristy, administrated by the Ottawa-Carleton Institute for Civil Engineering.

ISBN 0-612-07844-2

Canada

Name _____

Dissertation Abstracts International is arranged by broad, general subject categories. Please select the one subject which most nearly describes the content of your dissertation. Enter the corresponding four-digit code in the spaces provided.

SUBJECT TERM

SUBJECT CODE

U·M·I

Subject Categories

THE HUMANITIES AND SOCIAL SCIENCES

COMMUNICATIONS AND THE ARTS
Architecture 0729
Art History 0377
Cinema 0900
Dance 0378
Fine Arts 0357
Information Science 0723
Journalism 0391
Library Science 0399
Mass Communications 0708
Music 0413
Speech Communication 0459
Theater 0465

EDUCATION
General 0515
Administration 0514
Adult and Continuing 0516
Agricultural 0517
Art 0273
Bilingual and Multicultural 0282
Business 0688
Community College 0275
Curriculum and Instruction 0727
Early Childhood 0518
Elementary 0524
Finance 0277
Guidance and Counseling 0519
Health 0680
Higher 0745
History of 0520
Home Economics 0278
Industrial 0521
Language and Literature 0279
Mathematics 0280
Music 0522
Philosophy of 0998
Physical 0523
Psychology 0525
Reading 0535
Religious 0527
Sciences 0714
Secondary 0533
Social Sciences 0534
Sociology of 0340
Special 0529
Teacher Training 0530
Technology 0710
Tests and Measurements 0288
Vocational 0747

LANGUAGE, LITERATURE AND LINGUISTICS
Language
- General 0679
- Ancient 0289
- Linguistics 0290
- Modern 0291

Literature
- General 0401
- Classical 0294
- Comparative 0295
- Medieval 0297
- Modern 0298
- African 0316
- American 0591
- Asian 0305
- Canadian (English) 0352
- Canadian (French) 0355
- English 0593
- Germanic 0311
- Latin American 0312
- Middle Eastern 0315
- Romance 0313
- Slavic and East European 0314

PHILOSOPHY, RELIGION AND THEOLOGY
Philosophy 0422
Religion
- General 0318
- Biblical Studies 0321
- Clergy 0319
- History of 0320
- Philosophy of 0322

Theology 0469

SOCIAL SCIENCES
American Studies 0323
Anthropology
- Archaeology 0324
- Cultural 0326
- Physical 0327

Business Administration
- General 0310
- Accounting 0272
- Banking 0770
- Management 0454
- Marketing 0338

Canadian Studies 0385
Economics
- General 0501
- Agricultural 0503
- Commerce-Business 0505
- Finance 0508
- History 0509
- Labor 0510
- Theory 0511

Folklore 0358
Geography 0366
Gerontology 0351
History
- General 0578
- Ancient 0579
- Medieval 0581
- Modern 0582
- Black 0328
- African 0331
- Asia, Australia and Oceania 0332
- Canadian 0334
- European 0335
- Latin American 0336
- Middle Eastern 0333
- United States 0337

History of Science 0585
Law 0398
Political Science
- General 0615
- International Law and Relations 0616
- Public Administration 0617

Recreation 0814
Social Work 0452
Sociology
- General 0626
- Criminology and Penology 0627
- Demography 0938
- Ethnic and Racial Studies 0631
- Individual and Family Studies 0628
- Industrial and Labor Relations 0629
- Public and Social Welfare 0630
- Social Structure and Development 0700
- Theory and Methods 0344

Transportation 0709
Urban and Regional Planning 0999
Women's Studies 0453

THE SCIENCES AND ENGINEERING

BIOLOGICAL SCIENCES
Agriculture
- General 0473
- Agronomy 0285
- Animal Culture and Nutrition 0475
- Animal Pathology 0476
- Food Science and Technology 0359
- Forestry and Wildlife 0478
- Plant Culture 0479
- Plant Pathology 0480
- Plant Physiology 0817
- Range Management 0777
- Wood Technology 0746

Biology
- General 0306
- Anatomy 0287
- Biostatistics 0308
- Botany 0309
- Cell 0379
- Ecology 0329
- Entomology 0353
- Genetics 0369
- Limnology 0793
- Microbiology 0410
- Molecular 0307
- Neuroscience 0317
- Oceanography 0416
- Physiology 0433
- Radiation 0821
- Veterinary Science 0778
- Zoology 0472

Biophysics
- General 0786
- Medical 0760

EARTH SCIENCES
Biogeochemistry 0425
Geochemistry 0996
Geodesy 0370
Geology 0372
Geophysics 0373
Hydrology 0388
Mineralogy 0411
Paleobotany 0345
Paleoecology 0426
Paleontology 0418
Paleozoology 0985
Palynology 0427
Physical Geography 0368
Physical Oceanography 0415

HEALTH AND ENVIRONMENTAL SCIENCES
Environmental Sciences 0768
Health Sciences
- General 0566
- Audiology 0300
- Chemotherapy 0992
- Dentistry 0567
- Education 0350
- Hospital Management 0769
- Human Development 0758
- Immunology 0982
- Medicine and Surgery 0564
- Mental Health 0347
- Nursing 0569
- Nutrition 0570
- Obstetrics and Gynecology 0380
- Occupational Health and Therapy 0354
- Ophthalmology 0381
- Pathology 0571
- Pharmacology 0419
- Pharmacy 0572
- Physical Therapy 0382
- Public Health 0573
- Radiology 0574
- Recreation 0575
- Speech Pathology 0460
- Toxicology 0383

Home Economics 0386

PHYSICAL SCIENCES
Pure Sciences
Chemistry
- General 0485
- Agricultural 0749
- Analytical 0486
- Biochemistry 0487
- Inorganic 0488
- Nuclear 0738
- Organic 0490
- Pharmaceutical 0491
- Physical 0494
- Polymer 0495
- Radiation 0754

Mathematics 0405
Physics
- General 0605
- Acoustics 0986
- Astronomy and Astrophysics 0606
- Atmospheric Science 0608
- Atomic 0748
- Electronics and Electricity 0607
- Elementary Particles and High Energy 0798
- Fluid and Plasma 0759
- Molecular 0609
- Nuclear 0610
- Optics 0752
- Radiation 0756
- Solid State 0611

Statistics 0463

Applied Sciences
Applied Mechanics 0346
Computer Science 0984

Engineering
- General 0537
- Aerospace 0538
- Agricultural 0539
- Automotive 0540
- Biomedical 0541
- Chemical 0542
- Civil 0543
- Electronics and Electrical 0544
- Heat and Thermodynamics 0348
- Hydraulic 0545
- Industrial 0546
- Marine 0547
- Materials Science 0794
- Mechanical 0548
- Metallurgy 0743
- Mining 0551
- Nuclear 0552
- Packaging 0549
- Petroleum 0765
- Sanitary and Municipal 0554
- System Science 0790

Geotechnology 0428
Operations Research 0796
Plastics Technology 0795
Textile Technology 0994

PSYCHOLOGY
General 0621
Behavioral 0384
Clinical 0622
Developmental 0620
Experimental 0623
Industrial 0624
Personality 0625
Physiological 0989
Psychobiology 0349
Psychometrics 0632
Social 0451

UNIVERSITÉ D'OTTAWA
UNIVERSITY OF OTTAWA

ABSTRACT

This research is aimed at clarifying the mechanisms of strätlingite formation involved in hydration of the high alumina cement (HAC) - siliceous materials - water system, and development of a conversion-preventing additive for use in HAC.

Mechanisms of strätlingite (C_2ASH_8) formation in the high alumina cement (HAC) - siliceous material - water systems were investigated. Different siliceous materials, e.g. natural zeolites, silica fume, fly ash, ground granulated blast-furnace slag, and different sodium salts, e.g. sodium silicate, sodium sulfate, etc. were employed. Reactions between CAH_{10} or C_2AH_8 and dissolved silica occur. Acceleration of the silica dissolution by addition of chemical admixtures promoted the formation of strätlingite. The pH value of the HAC - siliceous materials - water system was also studied. The intrinsic relationship between the pH value and the potential for strätlingite formation is discussed. Mechanisms of strätlingite formation in preference to hydrogarnet (C_3AH_6) in HAC products are postulated. A method for prevention of strength reduction of HAC products due to the conversion of thermodynamically unstable hexagonal calcium aluminates to cubic hydrogarnet is described.

New conversion-preventing additives (CPA) to inhibit of hydrogarnet formation in HAC products are described. Compressive strength development of HAC mortars containing the CPA additive was studied. The effect of curing conditions on strength development was also investigated. No strength reduction occurs for the HAC/CPA mortar water-cured at 38 °C. Strätlingite preferentially formed in the HAC paste containing the CPA additive. Durability of inhibited HAC products is also studied. Conversion inhibited high alumina cement binders have excellent characteristics for corrosion protection of reinforcement under severe test conditions. The HAC/CPA mortar can effectively resist the penetration of chloride ions.

ACKNOWLEDGEMENTS

I am very grateful to my supervisor, Prof. J. J. Beaudoin, for his guidance, suggestions and support throughout this research.

Technical help from Dr. P. Grattan-Bellew in the x-ray diffraction analysis is also gratefully acknowledged. Great thanks belong to all the research and technical officers of the Materials Laboratory, Institute for Research in Construction, National Research Council Canada, where this research was conducted.

Thanks also belong to Mr. Yan Fu for his assistance in the course of this research.

The research was financially supported by NSERC and the Network of Centers of Excellence on High Performance Concrete.

CONTENTS

List of Tables

List of Figures

NOTATION

A ..... Al_2O_3;

C ..... CaO;

CH ..... $Ca(OH)_2$;

CPA ..... Conversion-preventing additive(s);

C_2ASH_8 ..... Strätlingite;

C_3AH_6 ..... Hydrogarnet;

EDXA ..... Energy dispersive x-ray analysis;

FA ..... Fly ash;

ggbs ..... ground granulated blast-furnace slag;

H ..... H_2O;

HAC ..... High alumina cement;

H-HAC ..... Pre-hydrated high alumina cement;

NZ ..... Natural zeolite;

S ..... SiO_2;

SEM ..... Scanning electron microscopy;

SF ..... Silica fume;

SM ..... Siliceous material(s);

XRD ..... X-ray diffraction.

Chapter 1

INTRODUCTION

- Background
- Objectives
- Scope

§1.1. BACKGROUND

High alumina cement (HAC) was invented in 1908 by J. Bied, a director of the Pavin de Lafarge company, France. Spackman was the first to obtain a U.S. patent for this material. Commercial HAC was produced by the Lafarge company in 1913. This cement is based upon calcium monoaluminate (CA). High early strength, good chemical resistance and the high temperature resistance of HAC products have encouraged the use of high alumina cement concrete in certain construction engineering applications. However, conversion of hexagonal calcium aluminate hydrates (CAH_{10} or C_2AH_8) to cubic hydrogarnet (C_3AH_6) in hydrated HAC concrete under certain temperature conditions has been a major problem limiting its use. The conversion process results in a densification of over 50% as the densities of CAH_{10} (1.72), and C_2AH_8 (1.95), are much less than those of C_3AH_6 (2.52). Consequently a significant reduction of strength during the service life of the concrete occurs. Many high alumina cement concrete structures built in the UK in the 1940's and 1950's collapsed due to later conversion. The British government as a direct result of those investigations issued a document entitled "High Alumina Cement Concrete in Buildings" on 20 July 1974. This document stated that "high alumina cement should not be used for structural work in buildings until further notice". The application of high alumina cement in structural members has been banned in virtually every country in the world.

The conversion process in the HAC system has been extensively studied. A HAC-based blended cement containing about equal amounts of HAC and granulated blast-furnace slag by mass was commercialized by the Building Research Establishment (BRE) with the trademark "BRECEM". It was promoted as a possible solution for prevention of the conversion reaction. This was attributed to strätlingite formation in preference to the hydrogarnet. Other additives such as silica fume and metakaolin have also been reported to favour the formation of strätlingite when HAC is blended with an equal amount of these pozzolanic materials. These pozzolans are widely used in portland cement concrete. Blast furnace slag and silica fume are both industrial by products. Supply is already limited in some countries. The early strength of the blended cement systems is significantly reduced as a large amount of HAC is replaced. For example the 1-day strength of the HAC-slag system reaches only about 60% of the strength of the system containing HAC alone. Strength of the HAC-slag system increases slowly with time to a value approaching the one-day strength of HAC concrete when water-cured at 20 °C. Hydrogarnet still forms at 38 °C but no strength reduction occurs for HAC-slag blended cement concrete.

§ 1.2. OBJECTIVES AND SCOPE

§ 1.2.1 . Objectives

The objectives of this research:

(1) to investigate the factors controlling the formation of strätlingite in HAC systems;

(2) to clarify the role of strätlingite production in limiting formation of hydrogarnet in HAC products;

(3) to develop a commercially viable conversion-preventing additive for HAC products.

§ 1.2.2 . Scope

The research is divided into two parts:

(1) Investigation of the mechanism of strätlingite formation in HAC systems containing different finely divided siliceous materials.

Analytical methods including x-ray diffraction analysis (XRDA), scanning electron microscopy (SEM), and pH determinations were used to identify the hydration products formed under different curing conditions at various stages of the hydration process. Studies of the effect of alkali on strätlingite formation in HAC/siliceous materials systems were emphasized.

(2) Development of a conversion-preventing additive for HAC products.

Candidate conversion-preventing additives (CPA) comprising binary system containing silicious material from different sources, eg. zeolite, fly ash, silica fume, slag and metakoalin and one of several alkali salts were studied. The one-day compressive strength and subsequent strength development of HAC

mortars containing a CPA formulated from the different compositions were determined. Hydration temperature included a critical curing condition for the conversion reaction ie. water-curing at 38°C.

Selected engineering properties of conversion-inhibited HAC concrete were investigated. These were intended to provide a comparative basis for evaluating the practical viability of the modified materials.

Engineering properties, relevant to the application of chemically stable HAC concrete in areas requiring high-performance were be investigated. The work included an evaluation of the efficacy of modified HAC with respect to corrosion protection of reinforcement in environments containing chloride ions, chloride-binding characteristics, scaling resistance due to de-icing salts, and accelerated hardening behaviour.

Chapter 2

LITERATURE REVIEW

- Hydration of High Alumina Cement
- Blended High Alumina Cement System

§ 2.1 Introduction

High alumina cement (HAC) is made by fusing a mixture of aluminous and low in silica calcareous materials, and grinding the resultant product to a fine powder. J. Bied, at the Pavin de Lafarge Company, obtained a patent for high alumina cement in 1908. The original objective of the HAC invention was to produce a cementing material resistant to the sulfate attack. HAC and its products have many desirable characteristics superior to those of portland cement, such as rapid hardening, high chemical resistance and fire resistance. These encouraged the use of high alumina cement concrete in certain engineering applications. However, conversion of the hexagonal hydrates (CAH_{10}* or C_2AH_8) to cubic hydrogarnet (C_3AH_6) has been a major problem limiting its use. Conversion is responsible for the retrogression of strength and durability of HAC concrete. Many high alumina cement concrete structures built in the UK in 1940's and 1950's collapsed due to later conversion. The British government as a direct result of those investigations issued a document on 20 July 1974, Ref. BRA. 1068/2, entitled 'High Alumina Cement Concrete in Buildings", to ban the use of HAC in structural members (Midgley, 1990).

Conversion reactions in hydrating high alumina cement concrete have been studied for many years. It is believed that high temperature and high relative humidity are critical for the conversion reaction to occur in high aluminate cement products.

Water/cement ratio is the most important parameter controlling the strength reduction after conversion takes place (Lea, 1970). The effect of water/cement ratio on the compressive strengths of both converted and unconverted high alumina cement concrete is shown in Fig. 2.1.

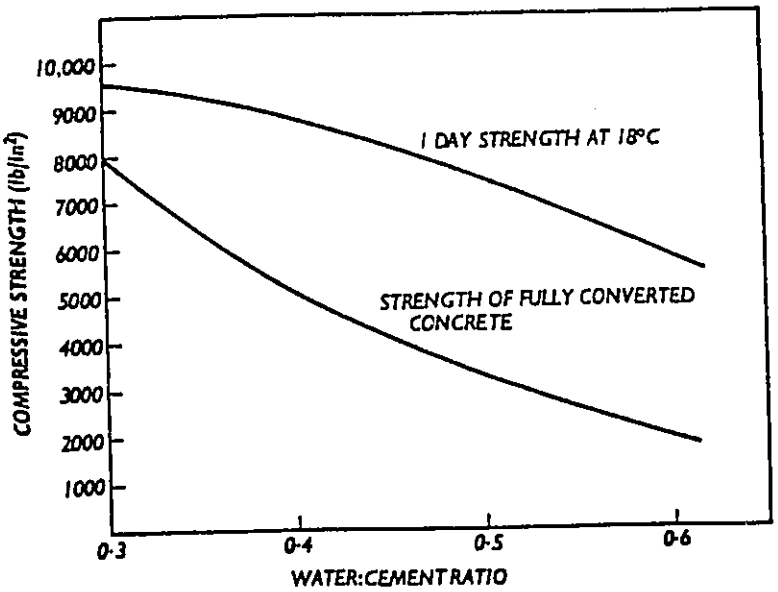


Fig. 2.1. Effect of water/cement ratio on converted and unconverted HAC concrete (Lea, 1970).

It is clear that the use of high water/cement ratio results in severe reduction of compressive strength in HAC concrete. It has been recommended that the HAC concrete be mixed with a water/cement ratio not greater than 0.4 and a minimum cement content 400 Kg/m^3 (Midgley, 1990). Minimizing the water/cement ratio appears to be a solution to limit the adverse effect due to conversion. It is, however, difficult to achieve in practice. It is now well known that water/cement ratio in portland cement concrete can be significantly reduced by using superplasticizer. However, supperplasticizers cannot be effectively applied in the HAC concrete. Quon and Malhotra (1981) reported that superplasticizer performed poorly in high alumina cement products. The HAC concrete did not achieve desired flow characteristics and slump loss occurred very quickly in 20

minutes even at very high dosages. Many studies aimed at preventing conversion have been conducted. There have not been successful. It is extremely difficult to prevent phase changes from the thermodynamically unstable hexagonal hydrates to stable hydrates. George (1990) concluded that, "The approach to aluminous cement concrete that seeks to avoid conversion is unrealistic".

Research at the Building Research Establishment (BRE) has attempted to eliminate the conversion by blending large amounts of ground granulated blast-furnace slag (ggbs) in HAC. Strength reduction associated with conversion was apparently prevented in an HAC concrete containing equal amounts of HAC and ground granulated blast - furnace slag (ggbs). However, the one-day strength of the HAC/ggbs concrete is significantly reduced compared to plain HAC concrete (Majumdar, 1990).

§ 2.2. Hydration of High Alumina Cement

Ciment Fondu. a high alumina cement produced by Lafarge Calcium Aluminates, Virginia, USA, has a typical range of chemical composition as listed in Table 2.1. (Taylor, 1990).

Table 2.1. The ordinary range of the oxide compositions of Ciment Fondu

Al_2O_3 %	CaO %	$FeO + Fe_2O_3$ %	FeO %	SiO_2 %	TiO_2 %	MgO %	$K_2O + Na_2O$ %	SO_3 %
38-40	37-39	15-18	3-6	3-5	2-4	<1.5	<0.4	<0.2

The hydration of high alumina cement is greatly influenced by temperature. The initial hydration product is mostly CAH_{10} at temperatures below 23°C. The initial hydration products consist mainly of C_2AH_8 at temperatures above 25°C. Hydrogarnet or C_3AH_6

becomes the dominant hydration product as the temperature approaches 35°C (Lea, 1970). CAH_{10} and C_2AH_8 convert to C_3AH_6 and AH_3 at a rate that depends on the temperature and other factors such as relative humidity. It was suggested (Quon and Malhotra, 1977) that the conversion rate in HAC concrete was a function of curing temperature regardless of the water/cement ratio. They concluded that the conversion rate was independent of the curing condition, i.e. water immersion, moist curing, or dry heat, etc. Taylor, however, concluded (1990) that CAH_{10} was the earliest product to be detected at both 5°C and 40°C. C_2AH_8 and AH_3 appeared to form by a dissolution precipitation mechanism involving CAH_{10}. C_3AH_6 and additional AH_3 appeared to form by a similar mechanism starting from C_2AH_8. Bradbury et.al.'s work (1976) also indicated that conversion occurred by a through solution mechanism. These processes are thermodynamically favored by the availability of free (liq.) water within the cement microstructure.

The specific volume of the hydration products of HAC and porosity of the cement paste is increased as a result of the conversion of hexagonal CAH_{10} or C_2AH_8 to cubic C_3AH_6 and AH_3. The strength of the cement paste is correspondingly reduced.

A number of studies have investigated alternative reaction paths for the hexagonal aluminates to overcome the strength reduction due to the conversion process. One approach involved addition of limestone to the HAC system. Wojciech (1990) reported that the use of limestone aggregate and $CaCO_3$ microfiller in HAC limited the conversion process. Revay, M. and Wagner,Z. (1985) indicated that carbonation of the HAC concrete that had undergone conversion was responsible for the strength increase. However, Midgley (1984) showed that cement made with HAC/$CaCO_3$ mixtures had lower strength potential than those made with HAC alone. Another approach involved

introduction of silica to the HAC system. Midgley and Rao (1978) showed that strätlingite, C_2ASH_8, had a strength giving property. Midgley (1980) reported that the small strength recovery after conversion is related to the presence of hydratable silicate minerals, i.e. pleochroite and beta -C_2S, in the HAC. The raw materials for HAC manufacture contain only a small amount of silica. Introducing more silica results in a large increase of gehlenite (C_2AS), an inert mineral, in HAC. This significantly diminishes the rapid-hardening characteristics of HAC (Taylor, 1964). It is therefore impractical to introduce sufficient reactive silicate mineral in HAC clinker because a high silica content in the raw material feed will result in the formation of the inert silicate mineral gehlenite (Taylor, 1990; Lea and Desch, 1956; Midgley, 1980). Midgley and Rao attempted to use hydrated portland cement as an additive for HAC cement to produce sufficient strätlingite however; it was not successful (Midgley and Rao,1978). A comparative study of the hydration of CA in the presence of C-S-H gel and of beta -C_2S with varying degrees of fineness was reported by Rao and Viswanathan (1980). They observed that the hexagonal aluminate hydrates could react with C-S-H gel to form strätlingite. The amount of strätlingite formed was dependent on the availability of C-S-H gel for reaction with the metastable aluminate hydrates. Extensive research on the HAC/ggbs blended system was carried out at the Building Research Establishment, UK. It is believed that the addition of a sufficient amount ggbs to HAC cement can effectively limit the conversion process (Edmonds and Majumdar, 1989; Majumdar, et. al.,1989).

§ 2.3. Blended High Alumina Cement System

§ 2.3.1. General

Extensive studies of blended high alumina cement systems were carried out at the British Research Establishment. Several silica-containing materials including blast-

furnace slag, fly ash, silica fume, metakaolin or Italian pozzolana were blended with high alumina cement. The range of HAC/silica-containing material varied from 40/60 to 60/40. The properties of these blended cement systems were reported by Majumdar and Singh (1992). The ggbs gave the most encouraging results. The HAC blends containing silica fume and metakaolin significantly reduced conversion, The one-day strength of these blended systems was however very low because more water was required for a suitable workability. The use of silica fume in combination of sodium tripolyphosphate as a defloculating agent in the HAC mortars was reported by Marcdargent et al. (1992). The sodium tripolyphosphate (TPP) improved workability and restricted strength reduction of the HAC/silica fume mortar (HAC/silica fume = 86/14; TPP/(HAC+silica fume) = 0.5) water-cured at 38 °C when very low w/c=0.3 was employed. The action of sodium tripolyphosphate in preventing the strength reduction in the HAC/silica fume mortar was not understood.

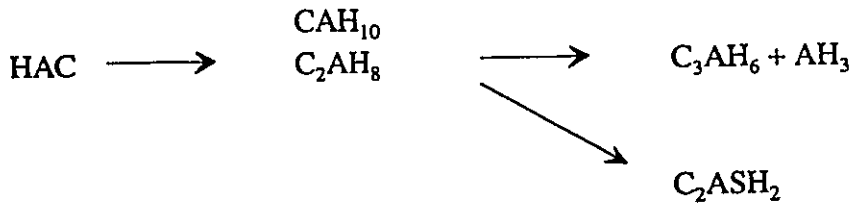
Addition of a sufficient amount of blast-furnace slag to an HAC concrete (HAC/ggbs=1/1 by mass) significantly modified the properties of the concrete. The initial temperature rise of the HAC/slag system was significantly reduced compared to the plain HAC material (Majumdar and Singh,1992). The strength reduction due to conversion was effectively eliminated in the HAC/ggbs concrete; the one-day strength was however significantly lower than the plain HAC concrete (Majumdar el. at., 1991, Majumdar el. at., 1990).

§ 2.3.2. Hydration of Blended High Alumina Cement System

Addition of silica-containing materials apparently alters the hydration of high alumina cement. The conventional conversion process, i.e. hexagonal aluminate hydrates to cubic hydrogarnet, is inhibited. A new reaction between the silica-containing materials

and hexagonal aluminate hydrates occurs resulting in the formation of strätlingite. Majumdar and Singh's work (1992) showed that a detectable amount of strätlingite was formed at later age in all the HAC/silica-containing materials investigated. Strength reduction still occurred in some blended systems. It is noted that strätlingite formation does not always compared to the elimination of strength. The XRD spectra for the HAC/slag paste and for the HAC/Italia pozzolana paste were similar; strätlingite was formed in both samples. The former showed no strength reduction; strength reduction occurred in the latter system. It appears the time of strätlingite formation is important to strength development. The availability of the reactive silica at an early age appears to be essential for strength to increase.

The hydration pattern in HAC/silica-containing materials system at 20-40°C range may be expressed as follows (Bentsen 1990; Fentiman and Rashid, 1990):



The extent that the reaction follows a particular paths is greatly influenced by the temperature. Detailed studies have been conducted on the hydration of HAC/slag and HAC/microsilica blended systems.

(1) HAC/ggbs blended cement systems:

Hydration of the HAC/ggbs blended cement systems has been widely studied. The amount of heat evolved during the first 24 hours hydration in a HAC/ggbs paste (HAC:ggbs=1:1 by mass) is much lower than in plain HAC (Majumdar and Singh,1992;

Singh and Majumdar, 1992). The major hydration product for HAC/ggbs system (ratio of HAC/slag >1) at temperatures between 20-40°C is strätlingite (Majumdar et.al.,1989 - 1992; Singh and Majumdar, 1992; Richardson and Groves,1990). A detailed study of the temperature effect on the hydration of the HAC/ggbs (1/1 by mass) system was made by Fentiman and Rashid (1990). They found that at 28 days the major hydration products at temperatures below 15°C, between 20 to 40°C and between 40 to 45°C were respectively CAH_{10}, C_2ASH_8, and C_3AH_6. The reactions involved in C_2ASH_8 formation were postulated as follows:

1. $2CAH_{10} \longrightarrow C_2ASH_8 + AH_3 + 9\,H$

2. $CAH_{10} + CSH \longrightarrow C_2ASH_8 + 3\,H$

3. $CAH_{10} \longrightarrow C_2ASH_8 + 2\,H$

4. $C_2AH_8 \longrightarrow C_2ASH_8$

5. $C_2AH_8 + 2\,CSH + AH_3 + 3\,H \longrightarrow 2\,C_2ASH_8$

6. $C_2AH_8 + AH_3 \longrightarrow 2\,C_2ASH_8$

C_3AH_6 was apparently not involved in a reaction to form C_2ASH_8. Higher temperature favored transformation of hexagonal aluminate hydrates (CAH_{10} C_2AH_8) to cubic hydrogarnet (C_3AH_6).

(2) HAC/microsilica blended cement systems:

A study of high alumina cement/microsilica blended cement (HAC/microsilica=10/7 and 1/1, by mass) was conducted by Bensten (1990, 1984). The major findings were as follows:

(a) Addition of microsilica in high alumina cement causes a reduction in the pH of the paste and the reactivity of CA.

(b) The lowest temperature for the formation of C_2ASH_8 appeared to be 20 °C. The upper limit appeared to be about 70 °C.

(c) The most probable reaction mechanism for formation of C_2ASH_8 is:

$$CA \longrightarrow \alpha\text{-}C_2AH_8 \longrightarrow \beta\text{-}C_2AH_8 \longrightarrow C_2ASH_8$$

$$CA_2 \longrightarrow AH_3$$

·Microsilica inhibits conversion to C_3AH_6 whether or not C_2ASH_8 or another silicate cement phase forms. Microsilica may influences the structure of C_3AH_6.

·The dominant phases in pure HAC and HAC - microsilica blended systems after 1-day and 1-week of hydration are as follows:

1-day (HAC):	0-20 °C	CAH_{10}
	20-50 °C	α–/β–C_2AH_8
	50-100 °C	C_3AH_6 & AH_3
1-week (HAC):	0-20 °C	CAH_{10}
	20-40 °C	α–/β–C_2AH_8
	40-100 °C	C_3AH_6 & AH_3
1-day(blended HAC-microsilica):	0-20 °C	CAH_{10}
	20-50 °C	α–C_2AH_8
	40-70 °C	C_2ASH_8
	70-100 °C	C_3AH_6 & AH_3
1-week (blended HAC-microsilica):	0-20 °C	CAH_{10}
	20-70 °C	C_2ASH_8
	70-100 °C	C_3AH_6 & AH_3

It is noted that the temperature range for the occurrence of C_2ASH_8 as a dominant phase in the HAC/microsilica system is greater than that in HAC/ggbs system. Formation of C_2ASH_8 and C_3AH_6 in blended system involves competitive reactions. The form of the dominant hydrate phase depends on the conditions of formation. The retardation effect of microsilica on HAC extents the time CAH_{10} or C_2AH_8 is present. An extended time period is available for the formation of C_2ASH_8. It is apparent that a large supply of reactive silica is favorable to the formation of strätlingite. There is a greater reactive silica content in the HAC-microsilica blended cement system (even for Microsilica/HAC = 0.7) than in HAC-slag system (HAC/slag = 1). This may partially explain the greater temperature range of strätlingite formation in the HAC-microsilica system.

Chapter 3

MECHANISMS OF STRÄTLINGITE FORMATION IN HIGH ALUMINA CEMENT - SILICEOUS MATERIAL SYSTEMS

- Hydration in the HAC - Sodium Silicate - Water System
- Strätlingite Formation in HAC - Silica Fume - Water System
- Significance of Sodium Ions on Strätlingite Formation

§ 3.1. Introduction

High early strength and good durability in aggressive environments have encouraged the use of high alumina cement (HAC) concrete in certain engineering applications. However, strength retrogression associated with conversion of hexagonal phases, CAH_{10} or C_2AH_8, to C_3AH_6 and AH_3 in hydrated HAC concrete, under certain environmental conditions, has been a major problem limiting its use. It was reported that the strength reduction of HAC concrete at later ages could be prevented with a large addition of microsilica or granulated blast furnace slag (ggbs) in HAC concretes. It is responsible to the preferential formation of strätlingite in stead of hydrogarnet in such a system. The conversion processes involving the thermodynamicle unstable hexagonal phases, CAH_{10} or C_2AH_8, to C_3AH_6 (hydrogarnet) and C_2ASH_8 (strätlingite) in hydrated HAC concrete are competitive.

The objective of this study is to clarify the mechanisms of strätlingite formation in HAC - siliceous material - water systems. Three systems were investigated: (1) HAC - sodium silicate - water system; (2) HAC - silica fume - sodium sulfate - water system; (3) HAC - silica fume, fly ash or ggbs - sodium sulfate - water system.

§ 3.2. Study of hydration mechanisms in the high alumina cement - sodium silicate system

§ 3.2.1. Experimental

Materials included Ciment Fondu, a high alumina cement (HAC), produced by Lafarge Calcium Aluminates, Virginia, USA; silica fume (containing SiO_2 95.17%, CaO 0.23%, Fe_2O_3 0.13%, Al_2O_3 0.21%, MgO 0.15%, SO_3 0.12%, Na_2O 0.10% and K_2O 0.27%) supplied by the SKW Co., Montreal, Canada; reagent grade sodium silicate

supplied by Silicates National Ltd, Toronto, Canada; and reagent grade calcium hydroxide. Mixes prepared for X-ray diffraction analysis of HAC pastes are listed in Table 3.1.:

Table 3.1. Mix Quantities for XRD Analysis of Cement Pastes (grams)

name	HAC	silica fume	sodium silicate	calcium hydroxide	water
MS-200	100	-	-	-	60
MS-202	100	-	-	1	60
MS-203	100	100	-	-	120
MS-204	100	100	-	1	120
MS-170	100	-	0.25	-	60
MS-169	100	-	0.5	-	60
MS-171	100	-	0.75	-	60
MS-194	100	-	1	-	60
MS-195	100	-	1.5	-	60

Cement paste samples having a high water/solid ratio (0.60) were used for XRD analysis. The major peaks associated with the strätlingite (C_2ASH_8) phase (d=1.26 nm), the C_2AH_8 phase (d=1.07 nm), the CA anhydrite phase (d=2.98 nm) and the hydrogarnet C_3AH_6 phase (d=2.04 nm) were monitored for all the samples. The test was designed for the comparison of parallel samples and is based on significant differences between them. The cement pastes were cast in plastic bottles (25 mm in diameter) and rotated on rollers for 24 hours at 25 °C. The hardened cement paste samples after demoulding were water-cured at 23 °C. The sample cut from the cylinders was ground in acetone and then scanned by XRD at designated ages. A Rigaku X-ray Diffractometer System Geigerflex

D/Max -B was used. Copper Kα radiation was employed. The peak height was calculated using Rigaku Standard Data Processing software.

The HAC pastes, with water/cement = 0.25 and sodium silicate contents, 0, 0.25, 0.5, 0.75, 1.0, 1.5% by weight of HAC, were prepared for determination of setting time and compressive strength. Setting was determined according to ASTM C 807-89. The compressive strength test was carried out on prism specimens (25x25x40 mm). The hardened paste specimens were water-cured at 23 °C.

§ 3.2.2. Results and discussion

The effect of silica fume on the strength of HAC paste has been studied by Majumdar and Singh (1992). The addition of silica fume resulted in a significant reduction of compressive strength of HAC paste. The candidate's unpublished results also confirmed that the one-day strength of HAC mortar containing 30% silica fume was only about 50% of the strength of plain HAC mortar when the water/solid (HAC + silica fume) ratio was the same. The retarding effect of microsilica on hydration of HAC was reported by Bentsen et al (1990). It was apparent that more unhydrated CA remained in the HAC paste containing microsilica than in plain HAC paste at early ages. They postulated that this retardation was due to the reduction in pH value in the HAC paste containing microsilica. It is known that the calcium hydroxide phase does not exist in HAC paste. Calcium hydroxide was reported to be one of the admixtures used to adjust setting time of high alumina cement (Murat and Sadok, 1990; Robson, 1962). The effect of calcium hydroxide on formation of C_2AH_8 in HAC paste is illustrated in the XRD spectra, Fig. 3.1. The addition of 1% calcium hydroxide by weight of HAC clearly reduces the formation of the C_2AH_8 phase (d-spacing 1.07nm) at 1 and 3 days age. The effect of calcium hydroxide on C_2AH_8 formation in HAC-silica fume paste (HAC/silica

fume = 1/1) is demonstrated by the XRD spectra, in Fig. 3.2. The effect of calcium hydroxide on plain HAC shown in Fig. 3.1 is opposite to that shown in Fig. 3.2. The addition of calcium hydroxide in HAC-silica fume paste accelerates C_2AH_8 formation. It appears that both calcium hydroxide and silica retard the hydration of pure HAC concrete. It is known that the addition of calcium hydroxide in HAC paste will result in quick setting of the paste (Robson, 1962). This is probably due to the quick formation of hydrated calcium aluminates on the surface of HAC particles when the system is rich in calcium ions. These quickly formed products surrounding the HAC particles prevent further hydration of the inner CA particles and retardation occurs. The retarding effect of silica is similar to that of calcium hydroxide. Microsilica can, to a limited extent, form soluble silica in the HAC-water system especially in presence of alkali. It has been argued that the pozzolanic reactivity of microsilica depends more on the nature of impurities e.g. alkali content, than on the fineness or SiO_2 content (Taylor, 1990). The dissolved silica will react with calcium ions released from HAC particles to form an insoluble calcium silicate (CSH) hydrate coating on the HAC particles and retard the further hydration of inner CA material. In the HAC-silica fume paste, additional calcium hydroxide would consume some dissolved silica to form CSH in the matrix and therefore reduce the concentration of dissolved silica in the system. The C_2AH_8 formation in this case would be more rapid than in the HAC-silica fume paste without additional calcium hydroxide.

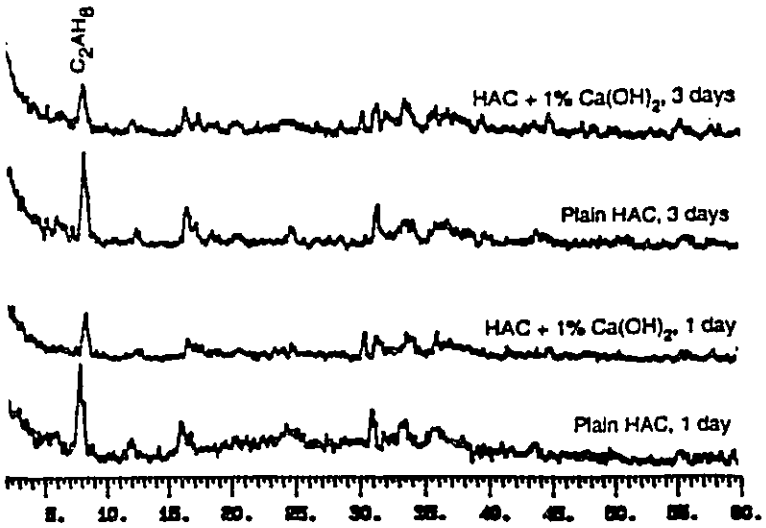


Fig. 3.1. Effect of $Ca(OH)_2$ on formation of C_2AH_8 in HAC paste during hydration.

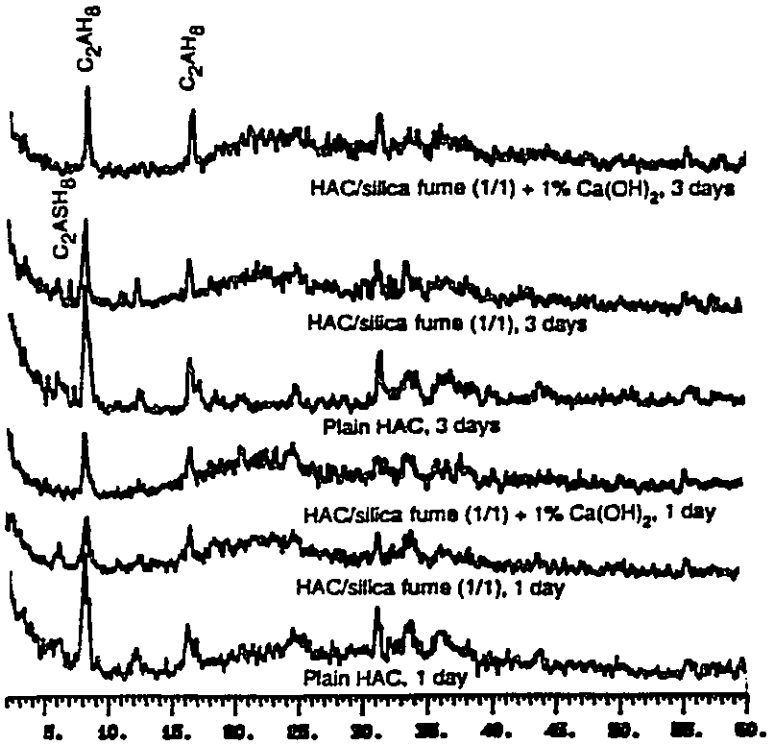


Fig. 3.2. Effect of $Ca(OH)_2$ on formation of C_2AH_8 in HAC-silica fume pastes during hydration.

Addition of sodium hydroxide to HAC paste is known to cause quick setting (Murat and Sadok, 1990; Robson, 1962). However, the addition of a small amount of sodium silicate apparently retards the setting time. The pH value of plain HAC paste is about 12; the pH values of HAC pastes containing sodium silicate and sodium hydroxide are higher. The effect of sodium silicate on the setting time of HAC paste is shown in Fig. 3.3. The setting time can be retarded by more than 48 hours for the HAC paste containing greater than 2% sodium silicate when the paste is rotated during hydration. This strongly retarded HAC paste can set in about one hour after adding 1% calcium hydroxide. Therefore, the pH of HAC paste may not be the only condition affecting setting time. It appears that (1) sodium ions may not contribute to the retarding mechanism; (2) silicate can strongly retard the HAC.

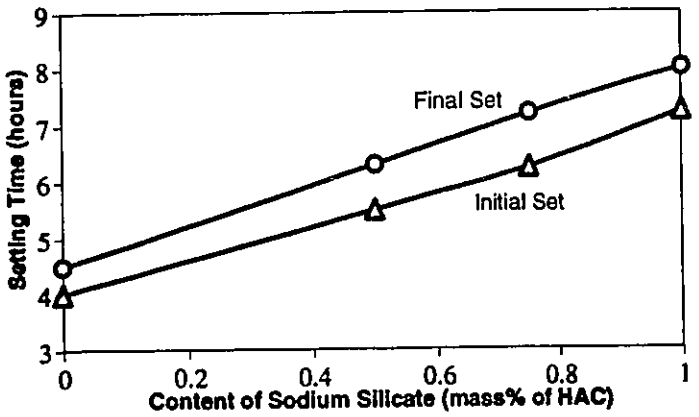


Fig. 3.3. Effect of sodium silicate on setting time of HAC paste.

The retarding effect of sodium silicate on HAC hydration was also reflected in the strength development curve (Fig. 3.4). The compressive strength of HAC paste at 1 day dramatically decreased with the addition of sodium silicate up to 0.5% by mass of HAC. Further reduction in strength was minimal when the addition of sodium silicate

was higher than 0.5%. Little effect of sodium silicate on 21-day compressive strength values was found. It appears that a small amount of sodium silicate may even enhance the compressive strength of HAC paste at later ages. Further research is required.

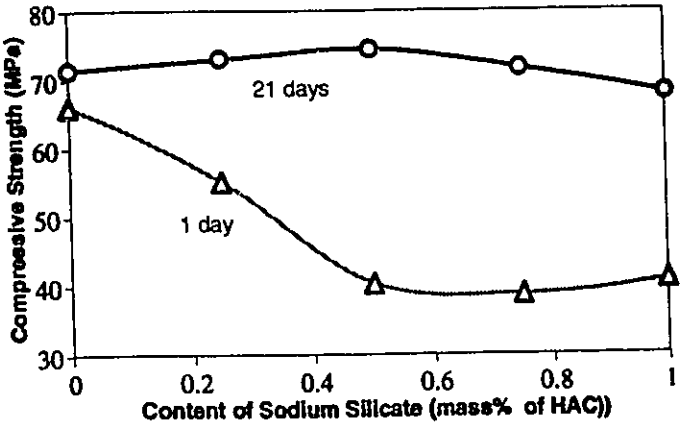


Fig. 3.4. Effect of sodium silicate on strength development of HAC paste.

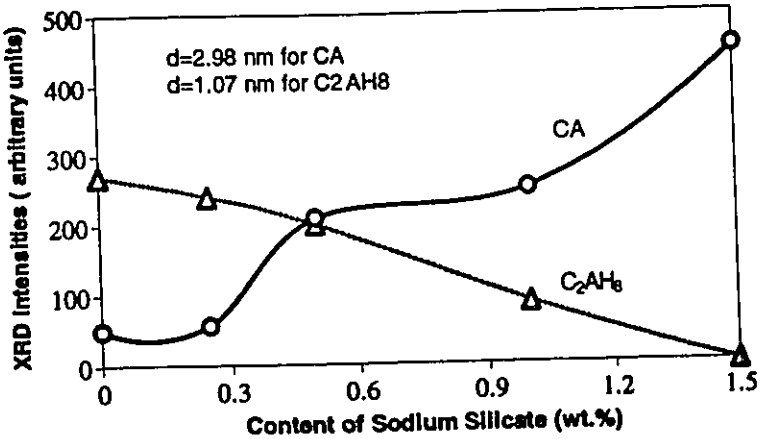


Fig. 3.5. Effect of sodium silicate (SS) on CA depletion and C_2AH_8 formation in HAC paste at 1-day.

X-ray diffraction analysis was used to identify phase formation during HAC hydration. The effect of sodium silicate on CA depletion and C_2AH_8 formation in HAC paste at 1-day is shown in Fig. 3.5. More CA remained and correspondingly less C_2AH_8 formed in HAC paste as sodium silicate addition increased from zero to 1.5%. No C_2AH_8 phase was detected in the HAC paste containing 1.5% sodium silicate at 1-day. CA

depletion with hydration time is illustrated in Fig. 3.6. CA was nearly all hydrated in the first day in plain HAC paste. The residual CA was eventually constant after 2 days. CA hydration was obviously delayed as sodium silicate was added. CA depletion in the HAC pastes containing sodium silicate reached an equilibrium state after 3-days hydration. An increase of sodium silicate clearly increases the retarding effect on CA hydration.

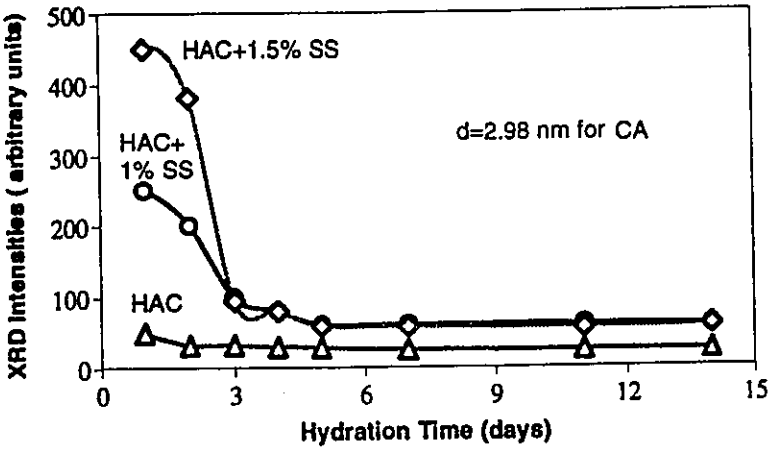


Fig. 3.6. Effect of sodium silicate (SS) content on CA depletion with hydration time in HAC Paste.

The effect of sodium silicate on the phase formation in HAC paste during hydration is shown in Fig.s 3.7 and 3.8. CA depletion and hydrate formation in plain HAC paste appear to be nearly complete after first day. The hydration of HAC paste was apparently delayed by addition of sodium silicate. CA depletion and C_2AH_8 formation occurred gradually in the first 5 days. The C_2AH_8 peak intensity then decreased with hydration time until about 12 days and reached an equilibrium state. Corresponding to this C_2AH_8 peak reduction, peaks for C_2ASH_8 and C_3AH_6 phases increased with hydration time. The XRD peak intensities of C_2ASH_8 and C_3AH_6 phases in HAC paste containing sodium silicate were apparently higher than those in plain HAC paste. The C_2ASH_8 formation in plain HAC paste resulted from the hydration of some minor silica-

bearing constituents in high alumina cement such as C_2AS and β-C_2S (Bentsen et. al.,1990; Robson,1962)

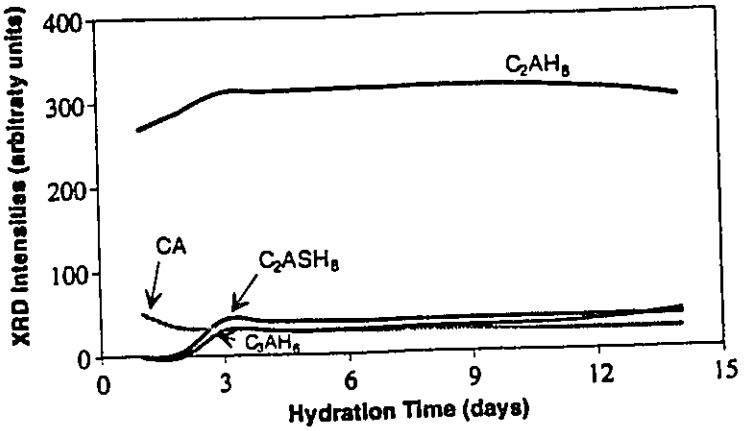


Fig. 3.7. Phase formation in plain HAC paste.

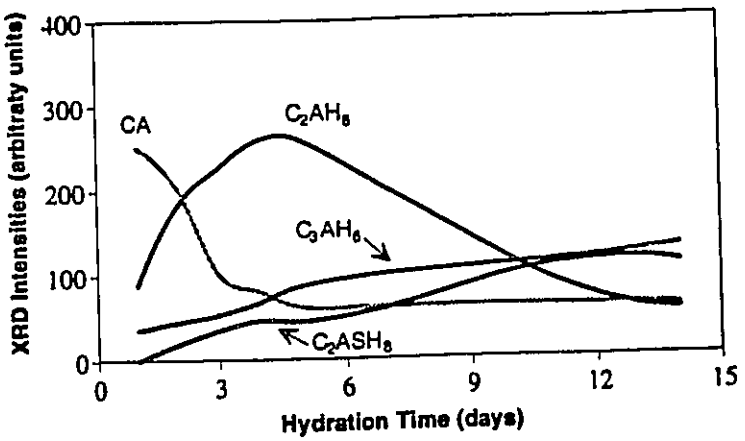


Fig. 3.8. Phase formation in HAC paste containing 1% sodium silicate.

The effect of sodium silicate content on the formation of C_2AH_8 and C_3AH_6 in HAC paste is shown in Fig.s 3.9 and 3.10, respectively. It is apparent that C_2AH_8 formation in plain HAC paste occurs mainly in the first day of hydration. Hydrogarnet phase (C_3AH_6) also was detected in plain HAC paste after 3 days hydration. No obvious change in C_3AH_6 peak intensity was found in the paste during 14 days hydration. The

C_2AH_8 formation rate in the HAC paste containing 1% sodium silicate was greatly retarded. The C_2AH_8 peak intensity gradually increased during the first five days hydration and then decreased. Corresponding to the decrease of C_2AH_8 peak intensity, the C_3AH_6 peak intensity increased continuously with hydration time. This relationship can also be found in the HAC paste containing 1.5% sodium silicate. The C_3AH_6 formation in the sample containing 1.5% sodium silicate was slower than that in the sample containing 1% sodium silicate. Little decrease of the C_2AH_8 peak intensity with hydration time was recorded from 5 to 9 days. A small amount of silicate addition appeared to lead to greater C_3AH_6 formation in the HAC paste even at normal temperature (e.g. 23 °C). This may be attributed to the effect of higher pH of the HAC paste by addition of sodium silicate (Robson, 1962). A larger amount of sodium silicate results in the formation of other hydration products, e.g. strätlingite, which might temporarily prevent the formation of C_3AH_6. C_3AH_6 formation was accelerated after 9-days hydration when the silicate had been consumed. The newly formed C_3AH_6 after 5 days hydration would appear to be converted from the C_2AH_8 phase since the amount of CA in the paste has reached an equilibrium state after 3 days hydration (Fig. 3.6).

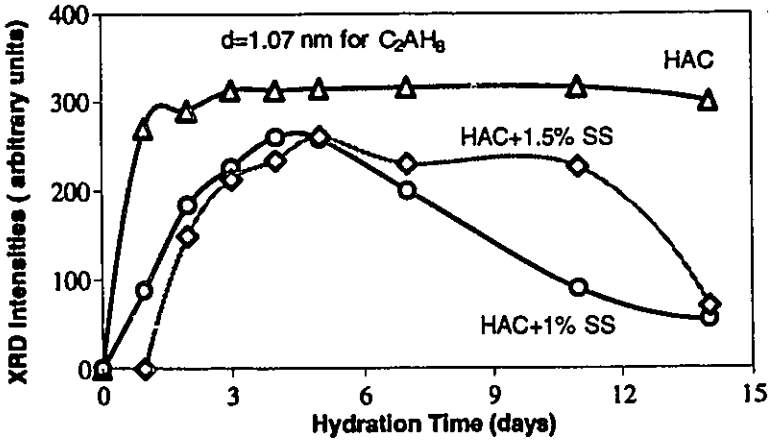


Fig. 3.9. Effect of sodium silicate (SS) content on C_2AH_8 formation in HAC paste during hydration

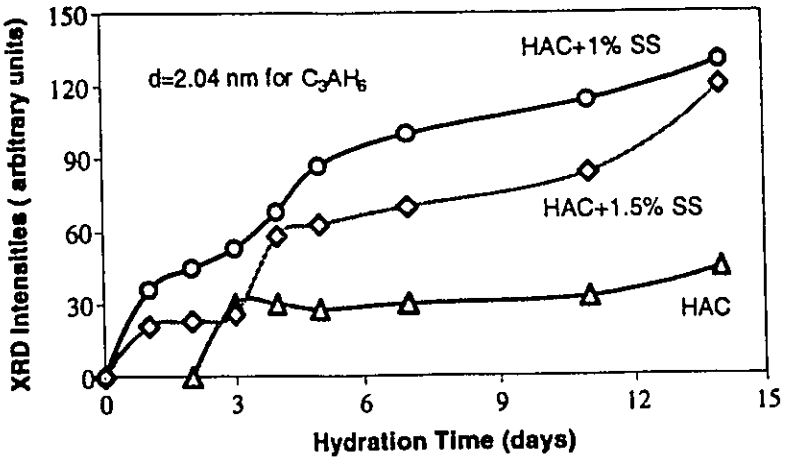


Fig. 3.10. Effect of sodium silicate (SS) content on C_3AH_6 formation in HAC paste during hydration.

The effect of sodium silicate content on formation of strätlingite is shown in Fig. 3.11. The strätlingite phase could be detected in HAC pastes after 1-day hydration. Its peak intensity in plain HAC paste reached a maximum value at 3 days and then remained nearly constant. The strätlingite peak intensities in the HAC pastes containing sodium silicate greatly increased after 5 days hydration. The intensity reached maximum value at about 10 days age. Increase of sodium silicate content in HAC paste apparently increases the formation of strätlingite.

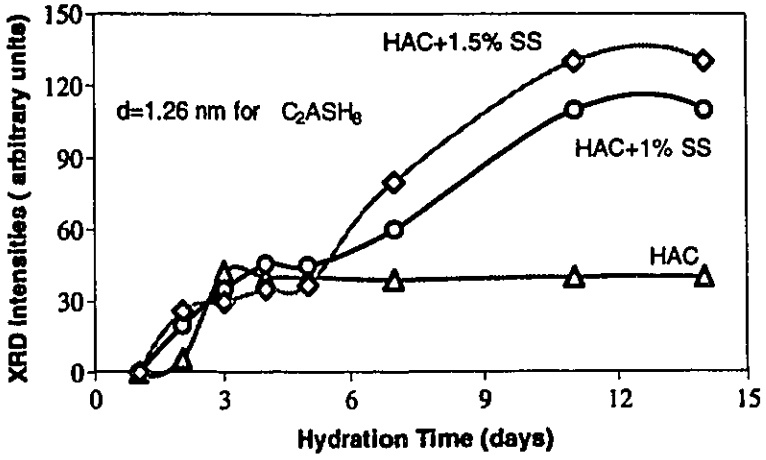


Fig. 3.11. Effect of sodium silicate (SS) on formation of strätlingite in HAC paste during hydration

Previous studies on the hydration of the HAC-microsilica system have indicated that the reaction between microsilica and HAC results in increased formation of strätlingite in preference to hydrogarnet. This research demonstrates that silicate plays a significant role in the mechanism of strätlingite formation in the HAC-microsilica system. Silica reacts to form silicates in high pH environment. This reaction is accelerated in presence of alkali ions. The alkali ions may probably act as a catalyst for reactions involving microsilica. Dissolved silicate anions then react with hydrated calcium aluminates (C_2AH_8 or CAH_{10}) to produce strätlingite. The reaction, in general, may proceed by a through solution mechanism. XRD analysis of HAC/silica fume paste samples shown in Fig. 2 appear to confirm this hypothesis. Peaks for the strätlingite phase appeared in the XRD pattern of HAC/silica fume paste sample at 3 days age. However strätlingite phase did not form in the same HAC/silica fume paste containing 1% additional $Ca(OH)_2$. Calcium hydroxide reacts with silica fume to form CSH and thus reduces the concentration of silicate anion in the HAC - microsilica - water system. This adversely affects strätlingite formation. Further studies on conversion prevention of aluminate phases in high alumina cement products are in process.

§ 3.2.3. Conclusions

Silicate addition can significantly retard the hydration of high alumina cement. This effect is probably one of the factors in the hydration of HAC - microsilica system that is responsible for very low early-strength. Addition of sodium silicate to HAC apparently promotes the formation of strätlingite. Strätlingite nucleation and crystallization appear to be dependent on the dissolved silica concentration in the HAC - microsilica system.

§ 3.3. Strätlingite formation in the high alumina cement - silica fume - water system

§ 3.3.1. Experimental

Materials included Ciment Fondu, a high alumina cement (HAC), produced by Lafarge Calcium Aluminates, Virginia, USA; Silica Fume supplied by the SKW Co., Montreal, Canada; reagent sodium sulphate. The oxide compositions of the HAC and silica fume are listed in Table 3.2.

Table 3.2. Oxide Compositions of HAC and Silica Fume

	Oxide Compositions (mass %)						
	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O+K_2O	SO_3
HAC	4.5	41.2	39.8	11.3	0.60	0.10	-
Silica Fume	95.17	0.21	0.23	0.13	0.15	0.37	0.12

HAC paste mixes prepared for X-ray diffraction analysis are listed in Table 3.3.:

Table 3.3. Mix Components of Cement Pastes prepared for XRD Analysis (grams)

Name	HAC	Silica Fume	Sodium Sulphate	Calcium Hydroxide	Water
MS-164	100	-	-	-	60
MS-71	100	30	-	-	78
MS-163	100	-	4.7	-	60
MS-72	100	30	4.7	-	78
MS-200	100	-	-	-	60
MS-202	100	-	-	1	60

Cement paste samples having a relatively high water/solid ratio (0.60) were used for XRD analysis. The major peaks associated with the strätlingite C_2ASH_8 phase (d=1.26 nm) and the hydrogarnet C_3AH_6 phase (d=2.04 nm) were monitored for all the samples. The test was designed for comparison of parallel samples. The comparison is based on significant differences between parallel samples. The cement pastes were cast in plastic bottles (25 mm in diameter) and rotated on rollers for 24 hours. The hardened cement paste samples after demoulding were cured in water. Some pastes (MS- 71, 72, 163 and 164) were cured at 38 °C and the others (MS- 200 and 202) were cured at 23 °C. The sample cut from the cylinders was ground in acetone and then scanned by XRD (degrees 2θ from 3 to 60°) at designated ages. A Rigaku X-ray Diffractometer System Geigerflex D/Max -B was used. Copper Kα radiation was employed. The peak height was calculated using Rigaku Standard Data Processing software. SEM micrographs were obtained using a Cambridge Stereoscan S250.

HAC mortars containing 2% sodium sulphate by mass of HAC were prepared for determination of compressive strength. The mixes are listed in Table 3.4.:

Table 3.4. Mix Components of Cement Mortar for Compressive Strength Test

(arbitrary mass units)

name	HAC	silica fume	sodium sulphate	SMF*	sand	water	water/solid** ratio
MS-1	1	-	-	-	2.75	0.4	0.40
MS-133	1	0.2	0.02	-	2.75	0.48	0.40
MS-105	1	0.3	0.02	-	2.75	0.60	0.46
MS-129	1	0.3	0.02	0.006	2.75	0.52	0.40

*SMF - superplasticizer, sodium sulfonated melamine formaldehyde; ** solid - HAC + silica fume.

The compressive strength test was carried out on cube specimens (50x50x50 mm). The specimens were moist-cured at 23 °C for 24 hours and then water-cured at 38 °C after demoulding.

§ 3.3.2. Results and discussion

Although microsilica is believed to promote strätlingite formation in HAC paste, it is still not able to prevent hydrogarnet formation (Majumdar and Singh, 1992). A significant change in the hydration of the HAC - silica fume system could be observed as sodium sulphate was added (Fig. 3.12). The HAC pastes (water-solids ratio = 0.6) were water-cured at 38 °C for 120 days.

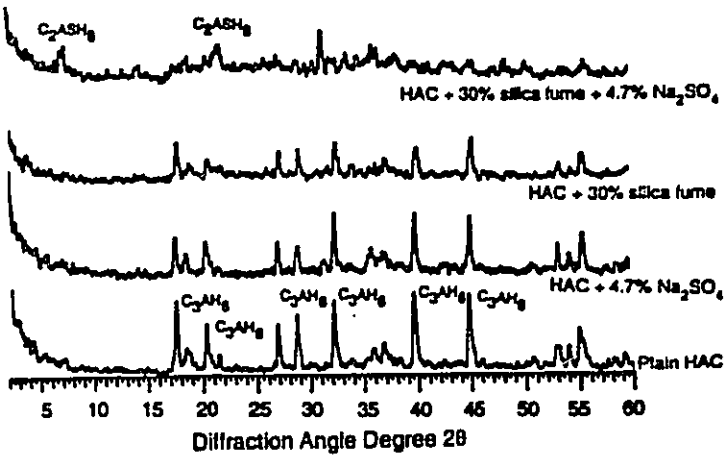


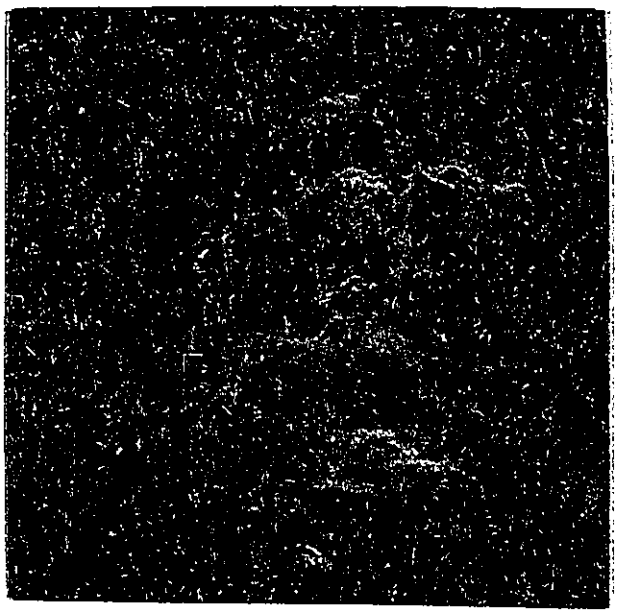
Fig. 3.12. XRD patterns for HAC/silica fume paste with or without sodium sulphate at 120 days age.

Very high intensity hydrogarnet peaks were recorded by XRD analysis of the plain HAC paste. Addition of sodium sulphate alone in HAC paste slightly reduces the peak intensities of the C_3AH_6 phase. Silica fume appeared to be more effective in reducing

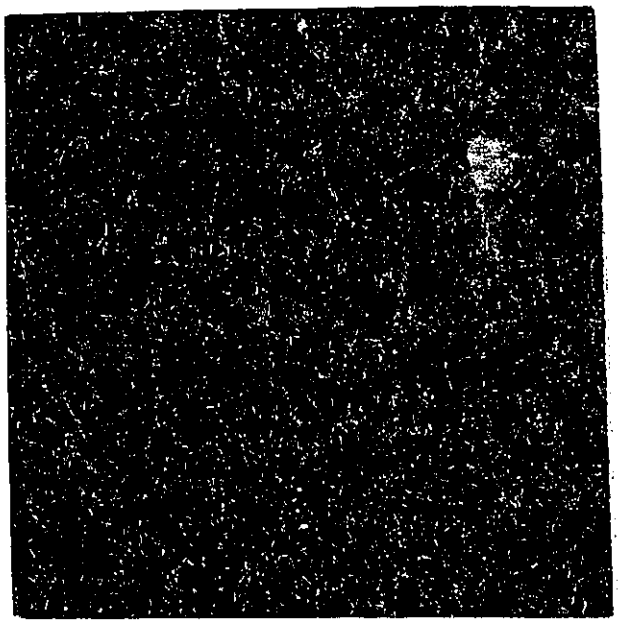
C_3AH_6 formation in HAC paste. It, however, does not eliminate the conversion. Hydrogarnet was still the major phase in the HAC/silica fume paste. Very little strätlingite phase was detected in these samples. The hydration process in HAC paste was essentially different as silica fume was added in combination with sodium sulphate. The hydrogarnet phase almost disappeared and strätlingite became the dominant phase in HAC/silica fume paste containing 4.7% sodium sulphate. Hydrogarnet, a stable product from the traditional conversion, was replaced by strätlingite.

The microstructure of HAC/silica fume pastes was examined by SEM analysis (Fig. 3.13). A large number of silica fume particles still remained in HAC/silica fume paste water-cured at 38 °C for 120 days (Fig. 3.13, a). It was found that these non-reacted silica fume particles resided on the surface of hydration products or were present in space between the hydration products (Fig. 3.13, b). This apparently weak structure may be responsible for the low strength of HAC/silica fume paste. The amount of unhydrated silica fume particles appears to be relatively less in HAC/silica fume paste containing 4.7% sodium sulphate (Fig. 3.13, c). Strätlingite plates were commonly found (Fig. 3.13, d). Addition of sodium sulphate apparently increased the reactivity of silica fume and promoted strätlingite formation.

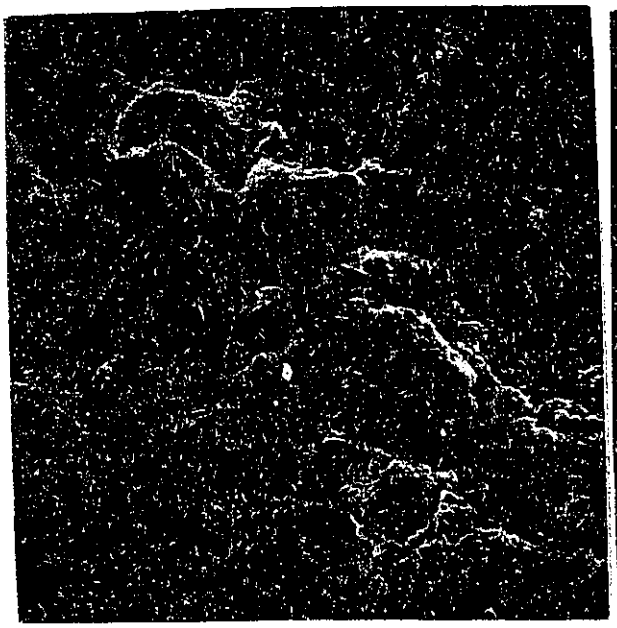
The significance of sodium salts in preventing strength reduction due to conversion is shown in Fig. 3.14. The compressive strength of plain HAC mortar was about 70 MPa at one-day. It, however, dropped to about 32 MPa at 14 days hydration. Little recovery of the strength then developed with the furtherhydration. The HAC mortar containing 20% silica fume and 2% sodium sulphate had relatively low compressive strength (about 28 MPa) at the first day. The strength then quickly increased to above 50 and 60 MPa at 14 and 28 days, respectively. The strength development after



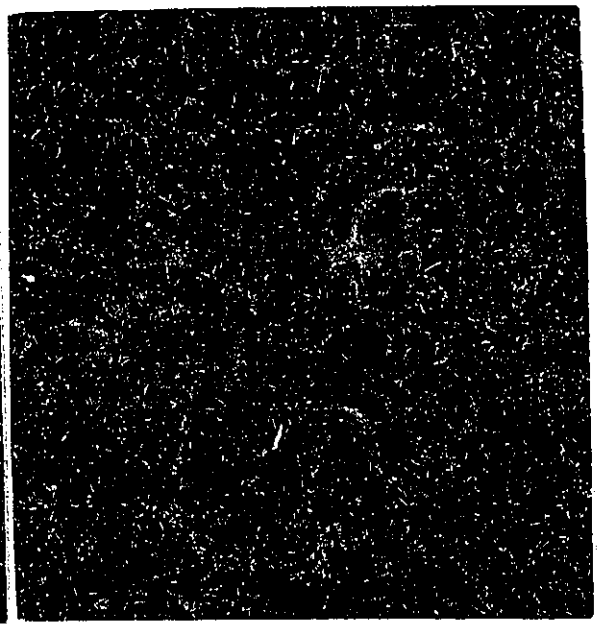
a. HAC/silica fume paste.
(w/s = 0.6, 120 days)



b. Silica fume on the surfaces of hydration products in HAC/silica fume paste.
(w/s = 0.6, 120 days)



c. HAC/silica fume paste containing 4.7% sodium sulphate.
(w/s = 0.6, 120 days)



d. Strätlingite plates in HAC/silica fume paste containing 4.7% sodium sulphate.
(w/s = 0.6, 120 days)

Fig. 3.13 c and d. SEM analysis for HAC/silica fume paste with or without sodium sulphate water cured at 38 °C for 120 days.

28 days was minimal. The increase of silica fume content to 30% in HAC mortar significantly decreases the 28-day strength. The reasons for this might be: (1) the corresponding increase of water/solid ratio requirement from 0.4 to 0.46 to satisfy workability as the silica fume content was increased from 20% to 30%; (2) the retarding effect of microsilica as reported by the authors (Marcdargent et. al., 1992); and (3) weak structure characterized by a large amount of unhydrated silica fume particles. Sodium sulfonated melamine formaldehyde, a superplasticizer, was used to reduce the water/solid ratio of HAC mortar containing 30% silica fume and 2% sodium sulphate. The HAC/silica fume mortars containing 20% or 30% silica fume and with the same water/solid ratio 0.4 had very similar strength development. This indicated that the addition of 20% silica fume and 2% sodium sulphate in HAC paste was sufficient to prevent significant strength reduction related to conversion. It is therefore relevant that addition of a small amount of sodium sulphate can effectively reduce the amount of silica fume in HAC required to achieve the same objective.

The effect of silica fume and sodium sulphate on hydrogarnet formation in HAC paste with hydration time is shown in Fig. 3.15. The peak intensity was calculated using Rigaku Standard Data Processing software. Small peak intensities (e.g. less than 50 Cps units) can be detected by the computer program; they may not be clearly shown in the spectra (see Fig.3.12), especially when the spectra were smoothed for presentation. Hydrogarnet in plain HAC paste cured at 38 °C mostly formed during the first day of hydration. Little change in the hydrogarnet peak intensities in plain HAC paste was found at later ages. Silica fume and sodium sulphate delay hydrogarnet formation for about 3 days, respectively. Hydrogarnet formation significantly reduced when both silica fume and sodium sulfate are added. The effect of calcium hydroxide addition on hydrogarnet formation in HAC paste is shown in Fig. 3.16. It is evident that the addition

of calcium hydroxide to HAC promotes the conversion process even at low temperature (23 °C). Wu et al. reported that relatively higher CaO concentrations in HAC stabilized crystalline hydrogarnet (Wu et. al., 1992).

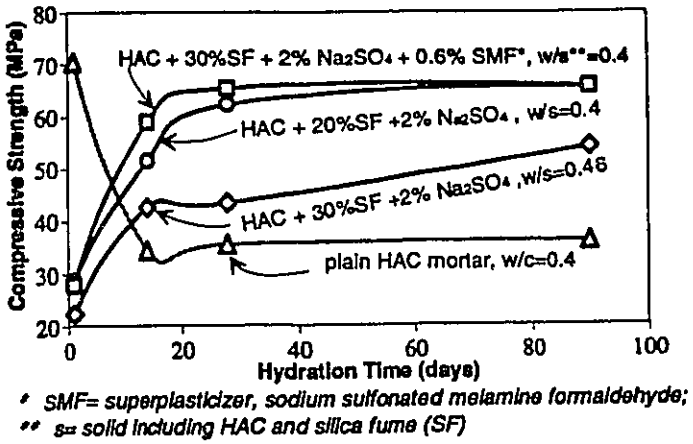


Fig. 3.14. Effect of sodium sulphate on strength of HAC/silica fume mortars (moist-cured at 23 °C in the first 24 hours and then water-cured at 38 °C).

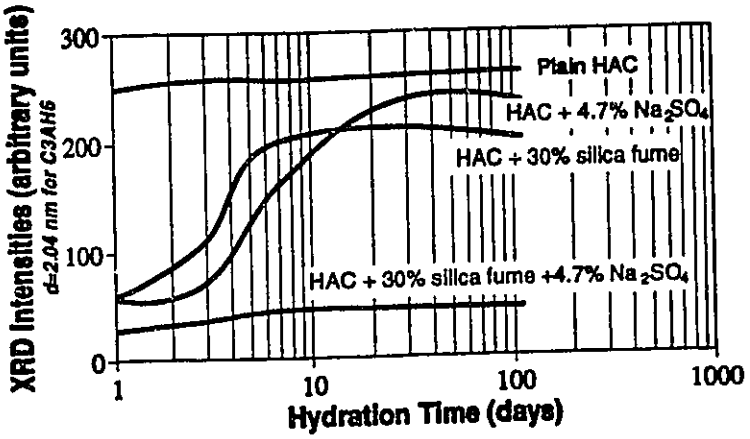


Fig. 3.15. Effect of silica fume and sodium sulphate on hydrogarnet formation in HAC paste water-cured at 38 °C for 120 days.

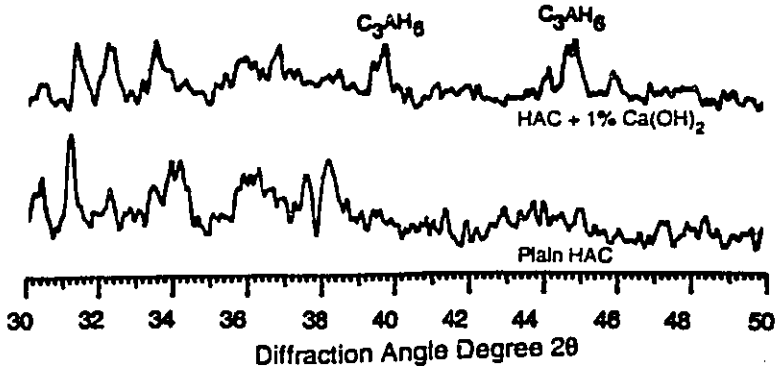


Fig. 3.16. Effect of calcium hydroxide on hydrogarnet formation in HAC paste moist-cured at 23 °C for 4 days.

The effect of silica fume and sodium sulphate on strätlingite formation in HAC paste with hydration time is shown in Fig. 3.17. As small peak at d=1.26 nm was detected in plain HAC paste water-cured at 38 °C at 3 days, which might be attributed to the formation of strätlingite. This x-ray peak intensity slightly increased until 10 days and then reached an equilibrium state. Silica fume slightly accelerates strätlingite formation at early ages. A small increase in intensity of strätlingite peaks was found in HAC paste containing silica fume compared to plain HAC paste. Sodium sulphate greatly accelerated strätlingite formation during the first day of hydration. The strätlingite peak intensities in HAC paste containing 4.7% sodium sulphate were finally the same as that in plain HAC paste since there were no additional silicate sources. Addition of silica fume in combination with sodium sulphate significantly increased strätlingite formation. The first day peak intensities of strätlingite in the HAC paste containing 30% silica fume and 4.7% sodium sulphate were about 50% greater than the ultimate peak intensities of strätlingite in the other samples. A large increase in strätlingite formation was found from 3 to 10 days. It has been postulated that sodium ions might play an important role in increasing the rate and amount of dissolution of silicate in the HAC system containing silica fume (Ding, et.al., 1994). This reaction mechanism may be operative in the period

of accelerated strätlingite formation. The equilibrium X-ray peak intensity of the strätlingite phase in such paste was about 3 times that in the other samples.

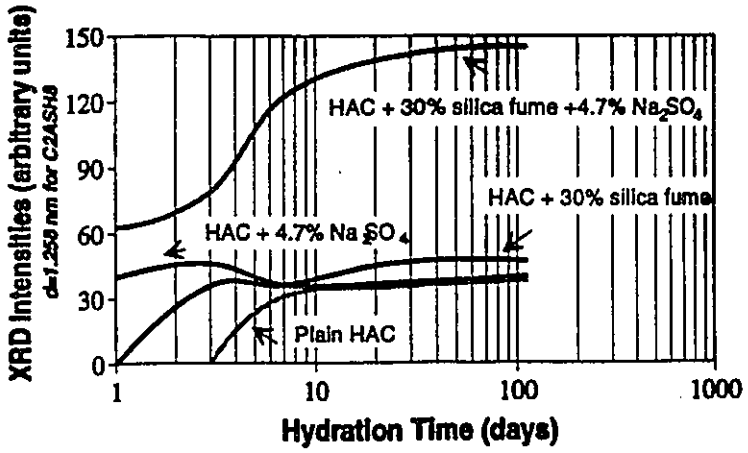
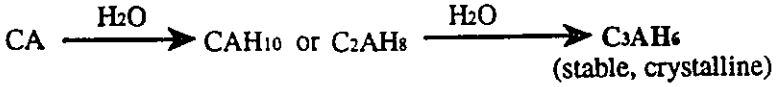


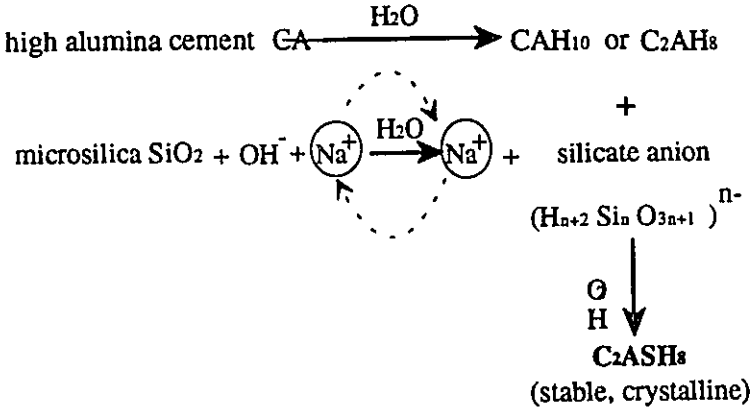
Fig. 3.17. Effect of silica fume and sodium sulphate addition on strätlingite formation in HAC paste water-cured at 38 °C for 120 days.

Hexagonal calcium aluminate hydrates in traditional HAC products are thermodynamically unstable. They generally convert to stable cubic hydrogarnet. In the absence of additional measures strength reduction of HAC products after conversion is likely to occur. The addition of silica fume in combination with a sodium salt in the HAC system alters the conventional conversion process. Metastable hydrates react with dissolved silica to form strätlingite rather than convert to different aluminates. Dissolved silica from microsilica promotes strätlingite formation in the HAC-microsilica system. Sodium ions play an important role in activating silica fume to form dissolved silica. The reaction mechanisms referred to above are briefly described as follows:

- **Classical conversion reaction in an HAC system:**



- **Modified conversion reaction in an HAC - microsilica - sodium salt system:**



§ 3.3.3. Conclusions

Sodium ions appear to play a significant role in strätlingite formation in HAC - silica fume systems. It is postulated that crystallization of strätlingite results from the reaction between CAH_{10} or C_2AH_8 and dissolved silica. Sodium ions promote increased dissolution of silica required for strätlingite formation. Hydration of silica fume in HAC paste without addition of sodium salt is very slow. Large amounts of unhydrated silica fume on HAC hydrate surfaces may result in low strength of HAC paste.

§ 3.4. Significance of sodium ions on strätlingite formation in high alumina cement - selected siliceous material - water systems

§ 3.4.1. Experimental

§ 3.4.1.1. Materials

1. High alumina cement (HAC), Ciment Fondu, produced by Lafarge Calcium Aluminates, Virginia, USA;
2. Silica fume, supplied by the SKW Co., Montreal, Canada;
3. ASTM Class F Fly ash;
4. Ground granulated blast-furnace slag (ggbs);
5. Sodium sulfate, reagent grade.

The oxide compositions of HAC and siliceous materials are listed in Table 3.5.:

Table 3.5. Oxide Compositions of HAC and Siliceous Materials

	Oxide Compositions (mass %)						
	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O+K_2O	SO_3
HAC	4.5	41.2	39.8	11.3	0.60	0.10	-
Silica Fume	95.17	0.21	0.23	0.13	0.15	0.37	0.12
Fly Ash	53.14	25.89	12.30	3.52	1.33	2.39	0.18
ggbs	35.37	10.49	36.66	0.96	13.40	-	1.50

§ 3.4.1.2. Sample Preparation

Twelve HAC slurries were made. They contained different siliceous materials in amounts of 0, 20, 50 and 100% by mass. Siliceous materials included silica fume, fly ash, and ground granulated blast-furnace slag (ggbs). In addition 0 and 4.7% sodium sulfate were added to each system. The w/s (s = HAC + siliceous material) was 2.75. The cement slurries were placed in plastic bottles (100 mL) and rotated on rollers (to prevent

hardening) at 38 °C. The pH value determination and XRD analyses were carried out at designated ages.

§ 3.4.1.3. Tests

(1) A Rigaku X-ray Diffractometer System Geigerflex D/Max -B was used for X-ray studies. Copper Ka radiation was employed. The peak heights were calculated using Rigaku Standard Data Processing software. The major peaks associated with the strätlingite (C_2ASH_8) phase (d=1.258 nm) and the hydrogarnet (C_3AH_6) phase (d=2.04 nm) were monitored for each sample. The test was designed for comparison between parallel samples.

(2) The pH value of the HAC/siliceous materials slurry systems were measured at 23 °C using an Orion pH/ISE meter, Model 720A.

(3) Scanning electron microscopy (SEM) was used to obtain micrographs of fracture surfaces using a Cambridge Stereoscan S250.

§ 3.4.2. Results

The effect of silica fume and sodium sulfate on strätlingite and hydrogarnet formation in the HAC slurries is shown in Fig. 3.18. Large peaks of hydrogarnet were detected by XRD in the plain HAC paste, HAC paste containing 4.7% sodium sulfate and HAC paste containing 50% silica fume. Strätlingite was not found in these samples. The presence of hydrogarnet was greatly reduced in the HAC paste containing both 20% silica fume and 4.7% sodium sulfate. It disappeared in this system when the silica fume content increased to 50%. Correspondingly, strätlingite formed in the samples containing silica fume in combination with sodium sulfate. In this case, the strätlingite peak intensities in the XRD spectra increased with silica fume content.

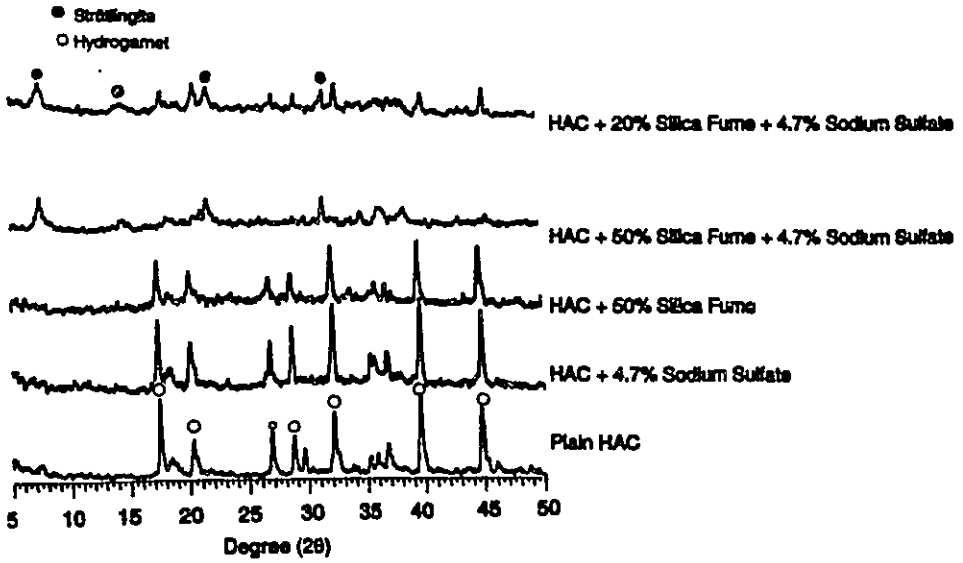


Fig. 3.18. XRD patterns for HAC/silica fume slurry; w/s=2.75, age=28 days.

The effect of fly ash on strätlingite and hydrogarnet formation in HAC slurries was similar to that of silica fume (Fig. 3.19). The use of 50% fly ash alone appeared to have no effect on the strätlingite and hydrogarnet formation. Addition of sodium sulfate in the HAC - fly ash system made the fly ash more effective in promoting strätlingite formation and preventing hydrogarnet formation.

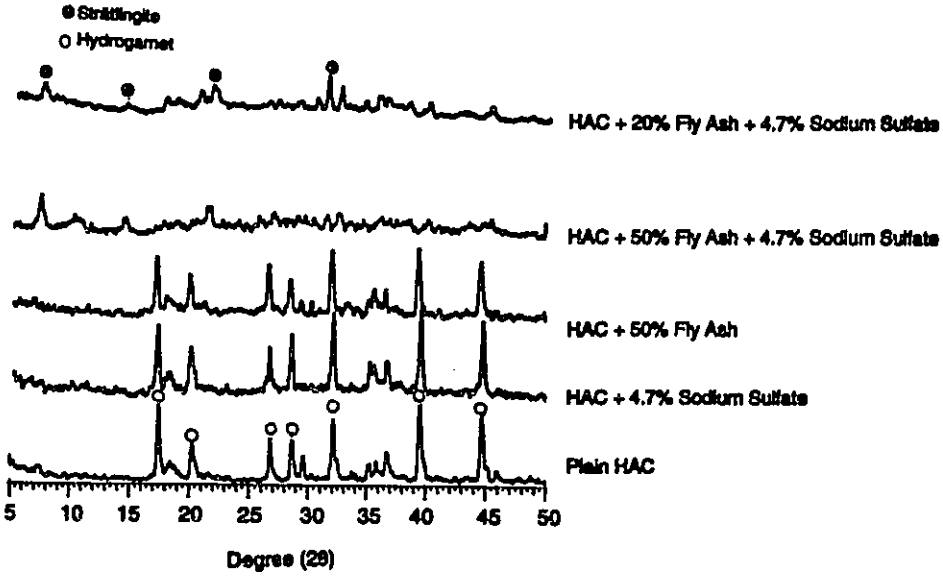


Fig. 3.19. XRD patterns for HAC/fly ash slurry; w/s=2.75, age=28 days.

Ground granulated blast-furnace slag (ggbs) itself appeared to favor strätlingite formation to a greater extent than the other siliceous materials (Fig. 3.20). Large strätlingite peaks were detected by XRD in the HAC paste containing 50% ggbs. Hydrogarnet, however, still formed in this sample. Addition of sodium sulfate to the HAC - ggbs system reduced the peak intensities of the hydrogarnet phase, but it was not as effective as in the HAC/silica fume or fly ash systems. Correspondingly sodium sulfate had little effect on further strätlingite formation.

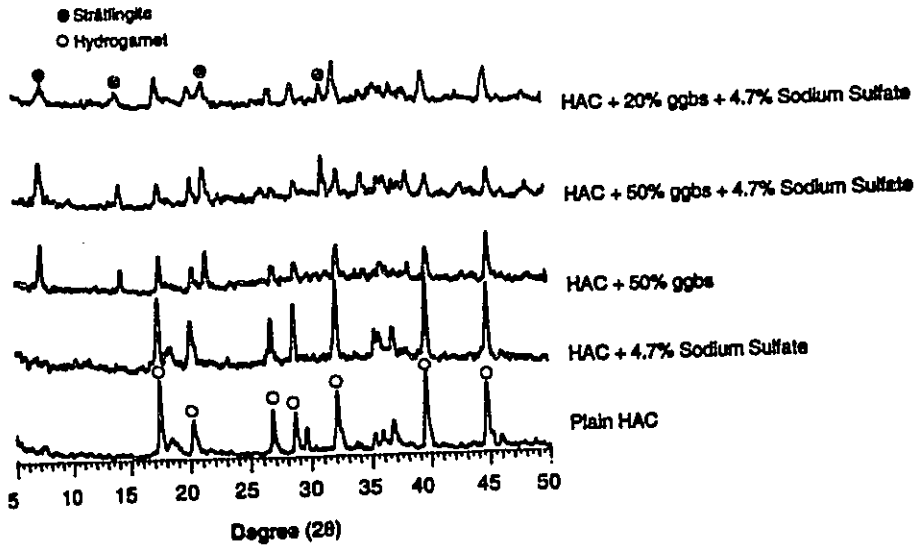


Fig. 3.20. XRD patterns for HAC/ggbs slurry; w/s=2.75, age=28 days.

The effect of ggbs, fly ash or silica fume content in the HAC slurries on the pH value of the system is shown in Fig. 3.21. Addition of ggbs increased the pH value of the HAC slurry from 11.73 (plain HAC) to 12.17. Addition of 20% fly ash increased the pH value of the HAC slurry from 11.73 to 11.95. This was followed by a slight decrease with the increase of fly ash content. Silica fume generally reduced the pH value of the HAC slurry. The pH value decreased with silica fume content. At high siliceous material contents, only ggbs can sustain a pH value higher than 12 without a sodium salt. Correspondingly, for the HAC - silica fume, fly ash or ggbs systems, XRD results

indicated that only the samples containing ggbs promoted strätlingite formation (Fig. 3.20.).

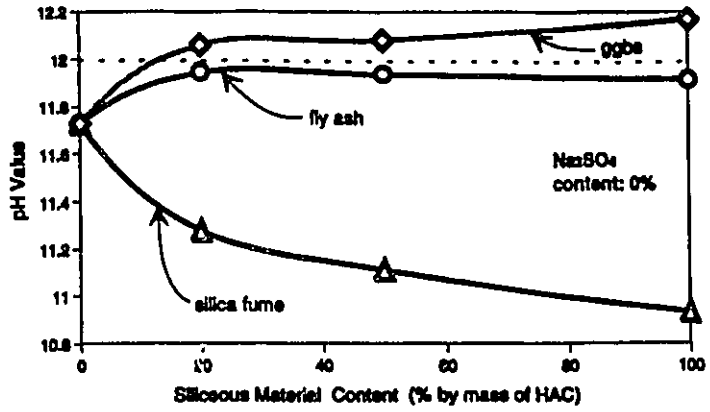


Fig. 3.21. Effect of siliceous material (SM) content on the pH value of HAC/SM slurry.

The effect of siliceous materials content of the HAC slurries containing 4.7% sodium sulfate on the pH value of the system is shown in Fig. 3.22. The pH value of HAC paste increased from 11.73 to 12.75 as sodium sulfate was added. The pH value of HAC slurry containing sodium sulfate increased from 12.75 (HAC + sodium sulfate) to 12.92 with 20% ggbs addition. This was followed by a slight decrease as ggbs content increases from 20 to 100%. The pH value of the HAC slurry containing sodium sulfate increased from 12.75 to 12.91 with fly ash content up to 50%, and then decreased greatly at 100% fly ash content. Silica fume generally reduced the pH value of the HAC slurry containing sodium sulfate. The pH value decreased with silica fume content in the HAC - sodium sulfate system similar to that in plain HAC slurry. The pH values of all the samples containing sodium sulfate were high than 12. XRD analyses indicated that strätlingite formed in all these samples.

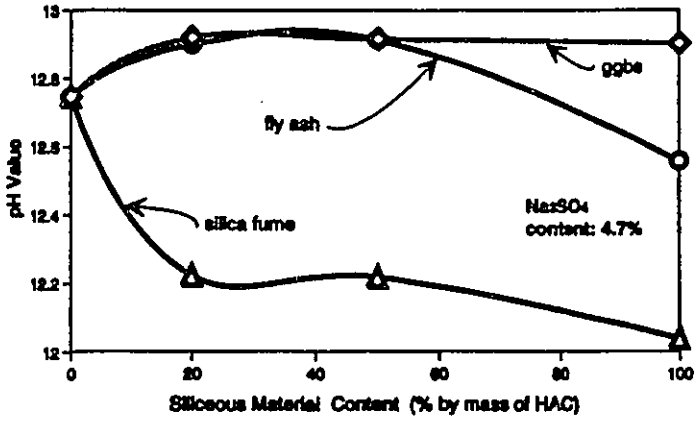


Fig. 3.22. Effect of siliceous material (SM) content on the pH value of HAC/SM slurry containing sodium sulfate.

§ 3.4.3. Discussion

Previous studies on the hydration of the HAC - siliceous materials systems have indicated that the reaction between siliceous materials and HAC results in increased formation of strätlingite in preference to hydrogarnet. The sodium ion appears to attack the silica crystal lattice and cause the pH value of the reaction system to be elevated. It plays a significant role in the mechanism of strätlingite formation in the HAC - siliceous materials system. Silica reacts to form silicates in a high pH environment. This reaction is accelerated in presence of alkali ions. The alkali ions probably act as a catalyst for reactions involving siliceous materials. Dissolved silicate anions then react with hydrated calcium aluminates (C_2AH_8 or CAH_{10}) to produce strätlingite. The reaction, in general, may proceed by a through solution mechanism. XRD analysis of HAC/silica fume paste samples shown in Fig. 3.15 appear to confirm this hypothesis. A large amount of strätlingite formed in the HAC paste only when siliceous material was added in combination with sodium sulfate. The XRD peak intensities for strätlingite in this sample were three times as high as in the other samples.

Hexagonal calcium aluminate hydrates in traditional HAC products are thermodynamically unstable at temperatures above 20°C. They generally convert to stable cubic hydrogarnet accompanied by strength reduction. The addition of silica fume in combination with a sodium salt in the HAC system alters the conventional conversion process. Metastable hydrates react with dissolved silica to form strätlingite rather than convert to different aluminates. Dissolved silica from siliceous materials promotes strätlingite formation in the HAC - siliceous materials systems. Sodium ions play an important role in activating silica fume to form dissolved silica.

Test results indicate that HAC slurries with pH value higher than 12 are conducive to increased strätlingite formation if siliceous material is added in sufficient amounts. This may be attributed to the reduction of AH_3 gel in the HAC paste when strätlingite forms in preference to hydrogarnet. Note that AH_3 is also one of the products of the conversion reaction:

$$3C_2AH_8 \longrightarrow 2C_3AH_6 + AH_3 + 9H$$

$$3CAH_{10} \longrightarrow C_3AH_6 + 2AH_3 + 21H$$

AH_3, i.e. alumina gel, is an amorphous compound; it has a high capacity to stabilize the pH of the system at a relatively low level. Research has shown that the pH value of the HAC - H_2O system will decrease after the conversion reaction take places and more gibbsite is formed. The pH value of HAC slurry (mainly comprising CAH_{10}) cured at 0°C was 12.57. The same sample was then placed at 38 °C for 24 hours. The pH value of the sample dropped to 11.95. It is postulated that (1) a pH value higher than 12 in HAC - siliceous materials system is a possible indicator of preferential formation of strätlingite; and (2) strätlingite can stably exist in an environment with a pH value higher than 12. Once strätlingite forms from the reaction between hexagonal calcium aluminates and

activated siliceous materials, the conversion reaction to form cubic hydrogarnet is inhibited.

§ 3.4.4. Conclusions

1. Strätlingite nucleation and crystallization appears to be dependent on the dissolved silica concentration in HAC - siliceous materials systems.
2. Sodium ions appear to play a significant role in strätlingite formation in the HAC - siliceous materials systems. It is postulated that crystallization of strätlingite results from the reaction between CAH_{10} or C_2AH_8 and dissolved silica. Sodium ions promote increased dissolution of silica required for strätlingite formation.
3. Addition of siliceous materials, such as silica fume, fly ash or ground granulated blast-furnace slag, in combination with sodium sulfate in HAC paste can prevent conversion from hexagonal calcium aluminates to cubic hydrogarnet when the paste is water cured at 38 °C.
4. Addition of sodium sulfate increases the pH value of the HAC - siliceous materials hydration system to values above 12.
5. A pH value higher than 12 is a potential indicator of strätlingite formation in HAC - siliceous materials systems.

Chapter 4

HYDRATION REACTIONS IN THE HIGH ALUMINA CEMENT - NATURAL ZEOLITE - WATER SYSTEM

- Strätlingite Formation Mechanisms
- pH Condition in HAC - Zeolite - Water System
- Stability of Hexagonal Calcium Aluminate Hydrates

§ 4.1. Introduction

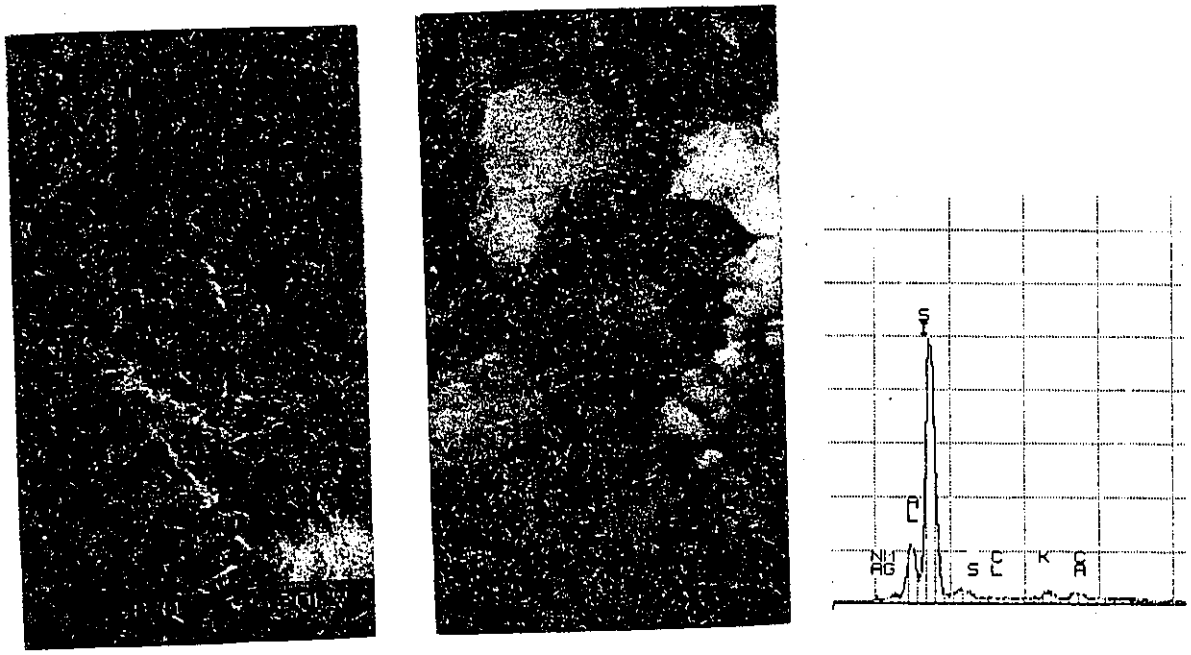
The conversion process in the HAC - water system is associated with phase changes of unstable hydrates to stable hydrates. Strätlingite forms as a stable hydrate when a reactive silica source is present in the HAC - water system. Industrial by products such as silica fume, granulated ground blastfurnace and fly ash combined with alkali ions are all effective in promoting formation of strätlingite. Natural zeolite has high pozzolanic activity and consistent properties. It is a porous silicoaluminate mineral and an attractive alternate silica source. Its structure consists of a three-dimensional framework of SiO_4 and AlO_4 tetrahedral. Natural zeolite would be ideal for industrial production of stable conversion-inhibited HAC. The reaction mechanisms of strätlingite formation during the hydration of HAC cement in presence of natural zeolites were of primary interest. Two systems were considered: (1) HAC slurry containing zeolite particulates and different sodium salts; (2) Zeolite slurry containing pre-hydrated HAC (H-HAC) particulates and different sodium salts. Samples in each system were separated into two parts after 2 months reaction: (1) particulate; (2) residual slurry. This process makes it possible to study the reactions involving H-HAC and zeolite individually.

§ 4.2. Experimental

§ 4.2.1. Materials

- High alumina cement: Ciment Fondu, containing SiO_2 4.5%, CaO 39.8%, Fe_2O_3 11.3%, Al_2O_3 41.2%, MgO 0.6%, Na_2O+K_2O 0.1%, produced by Lafarge Calcium Aluminates, Virginia, USA;

• Natural zeolite: containing mainly clinoptilolite, levyne and offretite minerals, supplied by Zeotech Corp., New Mexico, U.S.A. The SEM/EDXA analysis for the natural zeolite is shown in Fig. 4.1.



a. Fracture surface of zeolite. *b. Powdered zeolite.* *c. EDXA spectrum*

Fig. 4.1. The SEM/EDXA analysis for natural zeolite.

• Reagent chemicals: sodium sulphate, sodium silicate, sodium nitrate and sodium carbonate.

§ 4.2.2. Sample preparation

Pre-hydrated HAC: The HAC paste with w/c = 0.6 was cast in 25x25x150 mm steel moulds and cured at 0 °C for 28 days. XRD analysis indicated that the main phase in the H-HAC paste was CAH_{10} as shown in Fig.4.2.

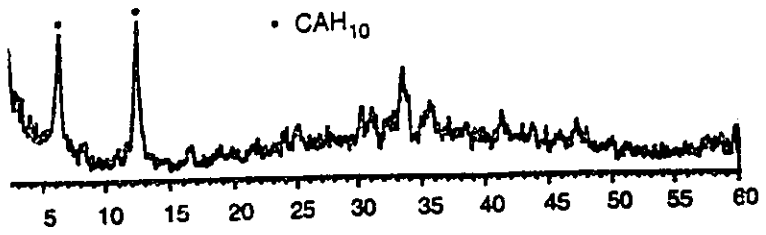


Fig. 4.2. The XRD pattern of H-HAC particulates

The H-HAC paste was then ground and sieved into particulates having particle size between 1.168 and 3.327 mm.

Natural zeolite: The natural zeolite rock was ground and sieved into two grades: (1) powdered zeolite having particle size less than 75 μm; (2) zeolite having particle size between 1.168 and 3.327 mm.

Sample mixes are listed in Table 4.1.

Table 4.1. Mixes (arbitrary mass units)

Samples	HAC	Particulate H-HAC	Powdered Zeolite	Particulate Zeolite	Admixtures
1	1	-	-	1	0.05 sodium sulphate
2	1	-	-	1	0.05 sodium silicate
3	1	-	-	1	0.05 sodium nitrate
4	1	-	-	1	0.05 sodium carbonate
5	-	1	1	-	0.05 sodium sulphate
1	1		1	-	0.05 sodium silicate
1	1		1	-	0.05 sodium silicate
7	-	1	1	-	0.05 sodium nitrate
8	-	1	1	-	0.05 sodium carbonate

Samples were placed in 100 ml bottles. The samples from No.1 to 4 (water/HAC ratio=3) were hydrated at 38 °C by rotating the bottles on a roller to prevent hardening. HAC slurry and zeolite particulates were separated by sieving each sample after 60 days reaction. Samples from No. 5 to 8 (water/zeolite ratio=3) were placed at 23 °C for 60 days. Zeolite slurry and H-HAC particulates were separated by sieving. The different

curing temperatures employed provided a more favorable condition for possible strätlingite formation in each system. In the first case, 38 °C favors strätlingite formation. In the second case, 23 °C was used to avoid quick conversion from CAH_{10} to C_3AH_6. If C_3AH_6 quickly forms and covers the surface of H-HAC particulates, reactions of the inner calcium aluminate phase with silicates from solution to form strätlingite will be restricted.

The samples used in this study were of two types: (1) HAC slurry containing zeolite particulates and different sodium salts; (2) Zeolite slurry containing H-HAC particulates and different sodium salts. Samples of each type were separated into two parts after 2 months reaction: (1) particulates; (2) residual slurry. The particulates were washed with water. The samples, i.e. slurries and particulates, were dried by vacuum in a desiccator at room temperature. Scanning electron microscopy (SEM) micrographs and energy dispersive x-ray analysis (EDXA) spectra were taken on the surface of particulates or dried slurry powder. Ground powder of the particulates or slurry was used for X-ray diffraction (XRD) analysis. A Rigaku X-ray Diffractometer System Geigerflex D/Max -B was used for X-ray studies. A Cambridge Stereoscan S250 Scanning Electron Microscope was employed for SEM/EDXA investigations.

§ 4.3. Results

§ 4.3.1. Particulate zeolite - HAC slurry - sodium salt systems

Zeolite Particulates

The XRD patterns, SEM photographs and EDXA spectra of the zeolite particulates are shown in Fig. 4.3. The XRD showed that little or no difference between the zeolite particulates, immersed in HAC slurries containing different sodium salts for 2 months. The mineral composition of these zeolite particulates was the same as the natural

zeolite. This indicated that no new reaction product formed on the zeolite particulates. It was clear in the SEM micrographs that the zeolite had a layered structure (Fig. 4.3.b, d and e). Zeolite particulates extracted from HAC slurries containing sodium silicate (Fig. 4.3.b.) or sodium nitrate (Fig. 4.3.e.) had clean surfaces. Small particles were found covering the surface of the zeolite particulates extracted from the slurries containing sodium carbonate (Fig. 4.3.c.) or sodium sulfate (Fig. 4.3.d). EDXA spectra indicated that these particles are rich in calcium. The silicon and calcium peak intensities on clean surfaces were similar to those of natural zeolite. The silicon peak intensities of the sample surfaces covered with the small particles were apparently lower than for the natural zeolite; the calcium peak intensities were much higher. Deposits of calcium carbonate or calcium sulfate, which have relatively low solubilities, might be responsible for this phenomenon.

HAC Slurries

The XRD patterns, SEM photographs and EDXA spectra of HAC slurries containing zeolite particulates and different sodium salts are shown in Fig. 4.4. High strätlingite peak intensities were found in the XRD patterns of HAC slurries containing sodium silicate (Fig. 4.4.a.) or sodium carbonate. The strätlingite peak intensity in the HAC slurries containing sodium sulfate or sodium nitrate was relatively low. A calcium aluminum oxide carbonate hydrate phase ($4CaO{\cdot}Al_2O_3{\cdot}CO_2{\cdot}11H_2O$) was found in the sample containing sodium carbonate. The SEM micrographs also showed more strätlingite plates in the first two samples than in the others (Fig. 4.4.b to e). Strätlingite plates were uniformly distributed among hydrogarnet (C_3AH_6) cubic particles. Dissolved silicates significantly affected the strätlingite and hydrogarnet formation. It was apparent that more strätlingite formed in the HAC containing sodium silicate than the others. A high pH value appeared to promote strätlingite formation. Sodium silicate and sodium

carbonate are highly basic salts. More strätlingite formed in these samples. Hydrogarnet still formed in the systems studied at 38 °C since the amount of dissolved silicate from zeolite particulates was limited. Addition of sodium silicate apparently promoted strätlingite formation and reduced hydrogarnet formation.

§ 4.3.2. Particulate hydrated HAC - zeolite slurry - sodium salt systems

Hydrated HAC Particulates

The XRD patterns, SEM photographs and EDXA spectra of hydrated high alumina cement (H-HAC) particulates after immersion in zeolite slurries containing different sodium salts are shown in Fig. 4.5. Strätlingite was detected in the particulates which had been immersed in zeolite slurries containing sodium silicate (Fig. 4.5.a.) or sodium carbonate for 2 months. The pH values of the zeolite slurries were determined by an Orion pH/ISE meter, Model 720A. The pH value of the zeolite slurries containing sodium silicate or sodium carbonate were 12.59 and 12.50 respectively. Stellerite ($2CaO{\cdot}2Al_2O_3{\cdot}14SiO_2{\cdot}14H_2O$) was detected instead of strätlingite growing on H-HAC particulates under lower pH conditions Samples were immersed in zeolite slurries containing sodium sulfate or sodium nitrate for 2 months. The pH values of these two slurries were 12.21 and 11.95 respectively. The CAH_{10} phase was present in all the samples after 2 months curing in a silicate-rich environment at 23 °C. No C_2AH_8 and C_3AH_6 was found. Ettringite formed on H-HAC particulates after immersion in zeolite slurry containing sodium sulfate. It is noted that ettringite only formed on H-HAC particulates (Fig. 4.5.d.), and not in the H-HAC slurry (Fig. 4.4.d.); the sulfate additions in these systems were the same. It has been reported that CAH_{10} forms ettringite more rapidly than other calcium aluminate hydrates (Fu, et. al., 1995). The particulate H-HAC mainly comprised CAH_{10}; ettringite might form from it at early ages. The effect of

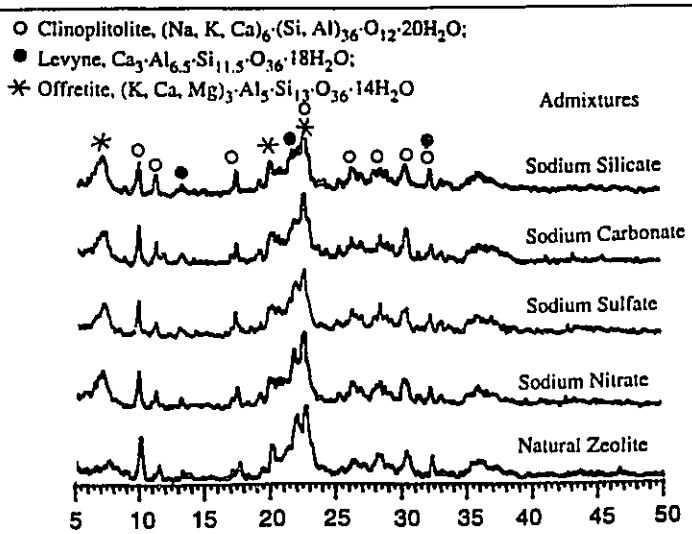
reaction site geometric location on ettringite nucleation/crystallization potential may also be a factor (Fu, et. al.,1994). The ettringite nucleation/crystallization potential is believed to increase in the following order:

in solution < on plate surfaces < in cracks

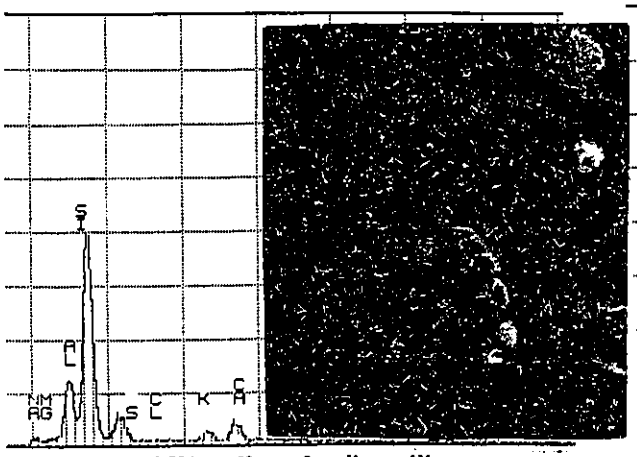
The SEM micrograph showed that needle-like ettringite crystals grew outward from the particulate surface. Plate-like crystals were present in all the samples. The large crystals might be hydrated calcium aluminate. They were sites for strätlingite or stellerite crystal growth. Strätlingite and stellerite have plate-like morphology. No cubic hydrogarnet crystals were found in the samples by SEM analysis.

Zeolite Slurries

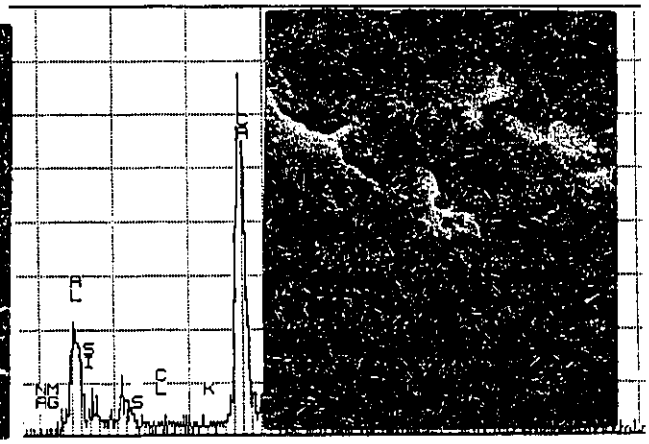
The XRD patterns, SEM photographs and EDXA spectra of zeolite slurries containing H-HAC particulates and different sodium salts are shown in Fig. 4.6. The XRD pattern showed that little or no difference was found between the zeolite slurries. The mineral compositions of the zeolite slurries were the same as that of natural zeolite as shown in Fig. 4.1. No new reaction product appeared to form in the zeolite slurries. The EDXA spectra showed similar characteristics for all the samples. The zeolite slurries were conglomerated after drying. No hexagonal-plate and other reaction products were identified in the SEM micrographs.



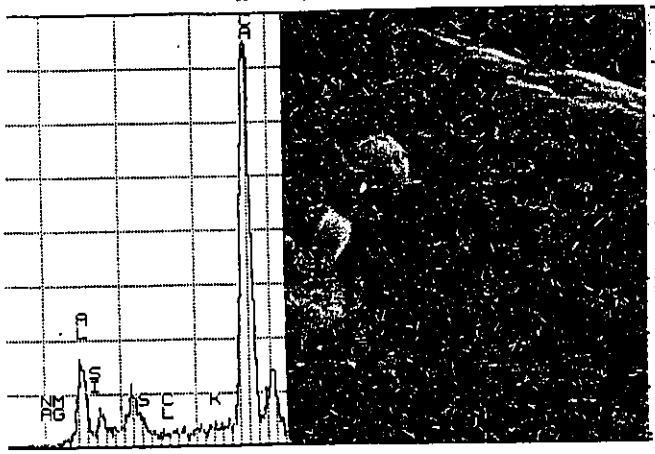
a. XRD Patterns



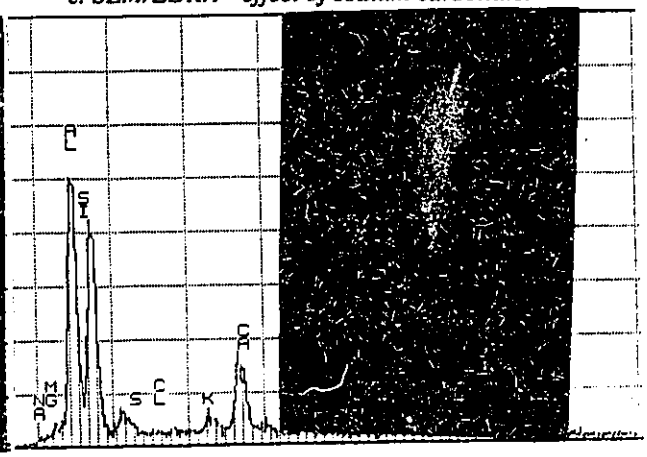
b. SEM/EDXA - effect of sodium silicate.



c. SEM/EDXA - effect of sodium carbonate.

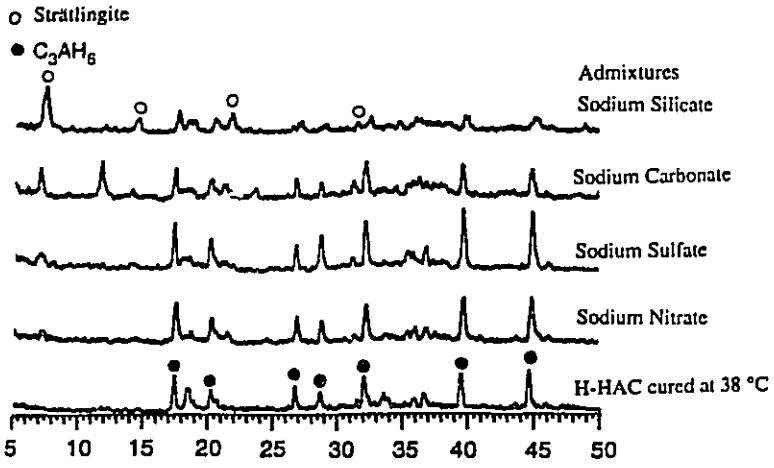


d. SEM/EDXA - effect of sodium sulfate.

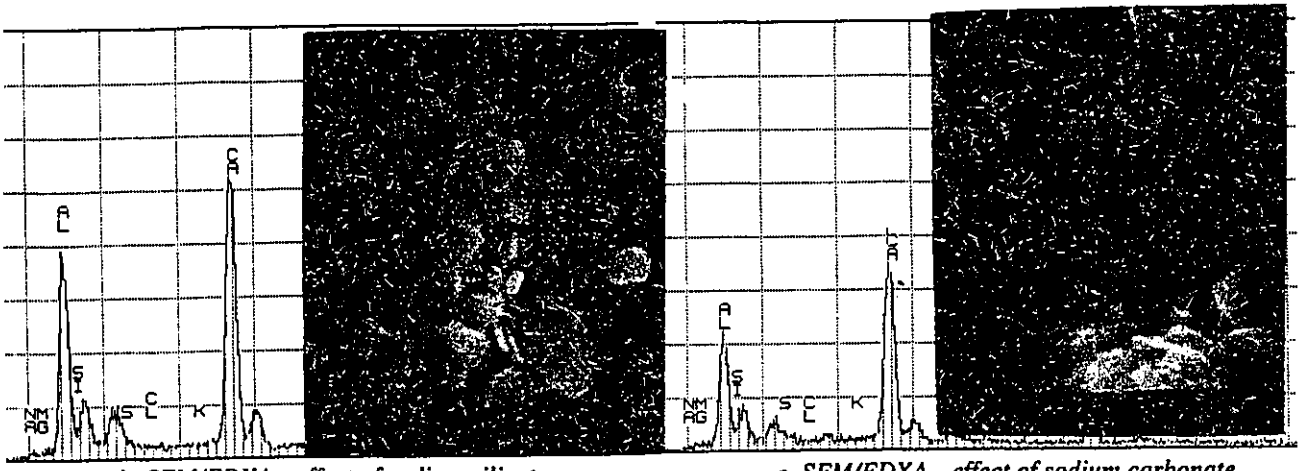


e. SEM/EDXA - effect of sodium nitrate.

Fig. 4.3. XRD and SEM/EDXA analysis of zeolite particulates after immersion in HAC slurries containing different sodium salts.

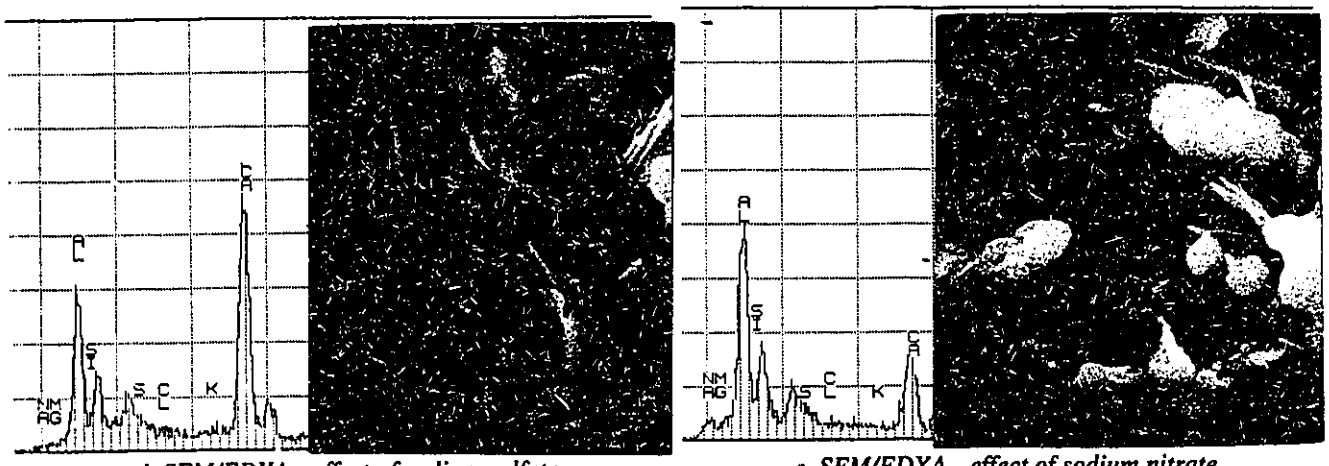


a. XRD Patterns



b. SEM/EDXA - effect of sodium silicate.

c. SEM/EDXA - effect of sodium carbonate.



d. SEM/EDXA - effect of sodium sulfate.

e. SEM/EDXA - effect of sodium nitrate.

Fig. 4.4. XRD and SEM/EDXA analysis of HAC slurries containing zeolite particulates and different sodium salts.

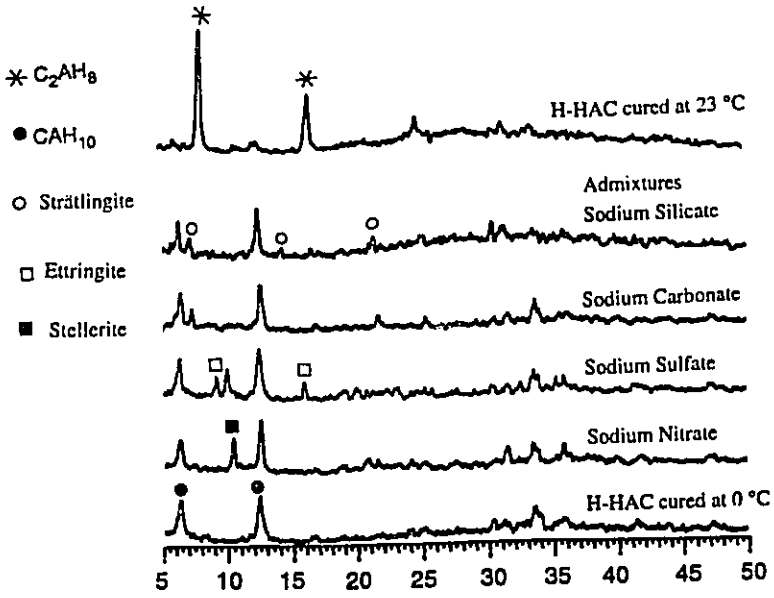
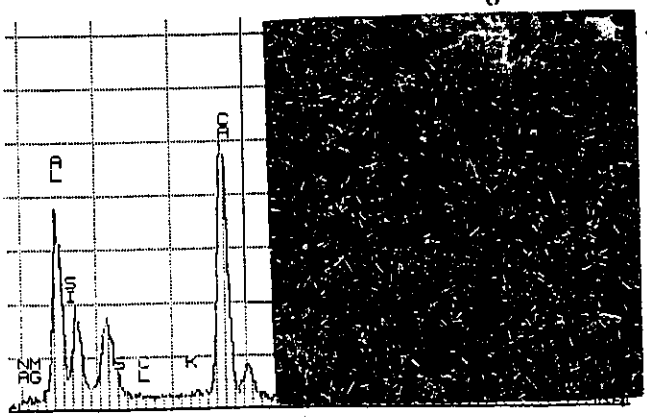
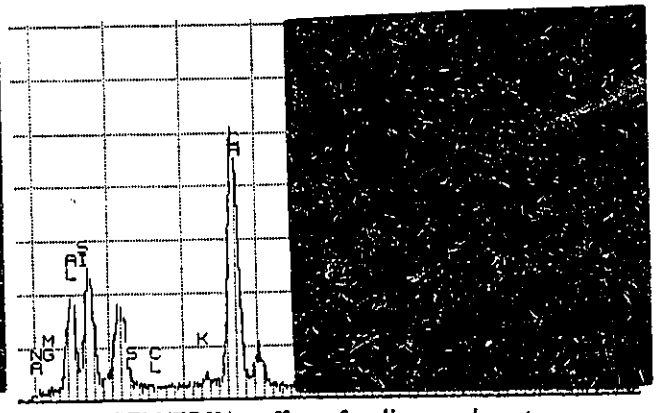


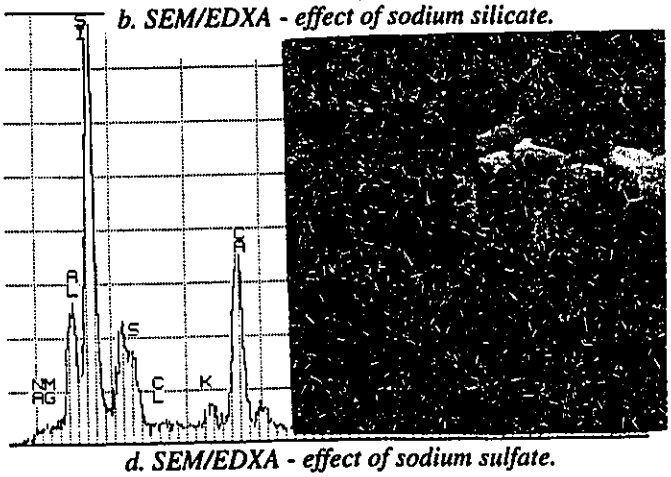
Fig. 3.5. a. XRD Patterns



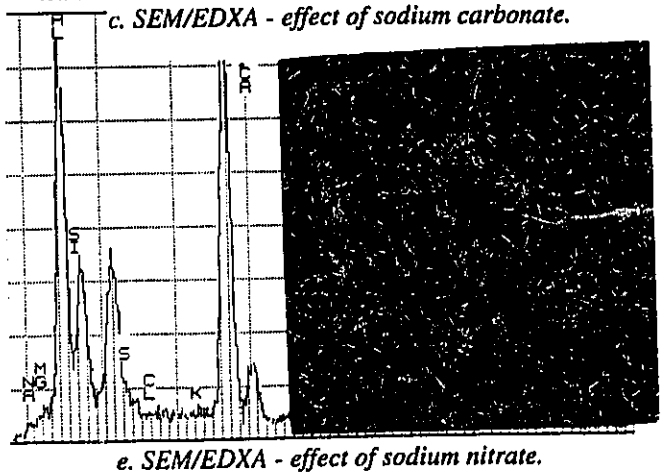
b. SEM/EDXA - effect of sodium silicate.



c. SEM/EDXA - effect of sodium carbonate.

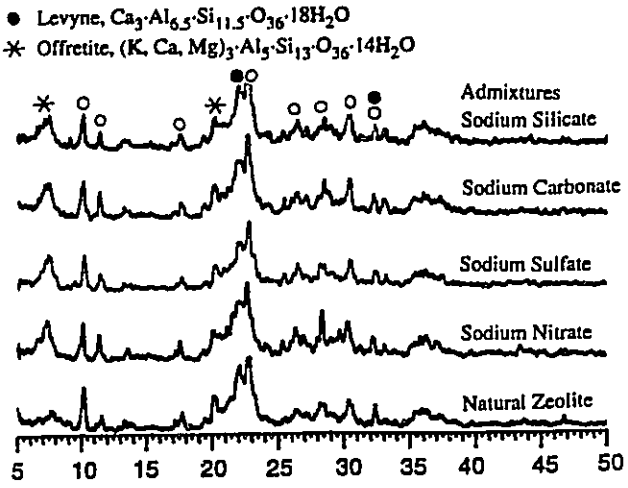


d. SEM/EDXA - effect of sodium sulfate.

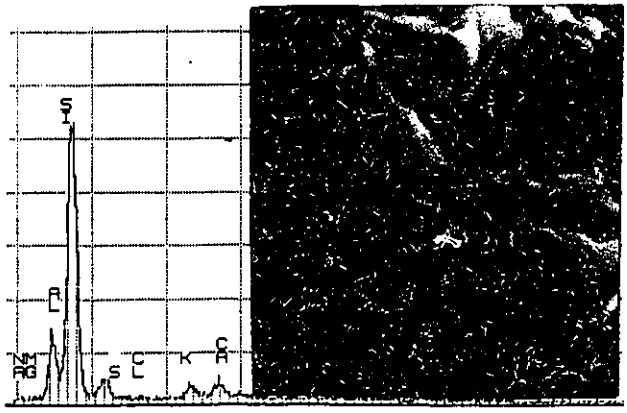


e. SEM/EDXA - effect of sodium nitrate.

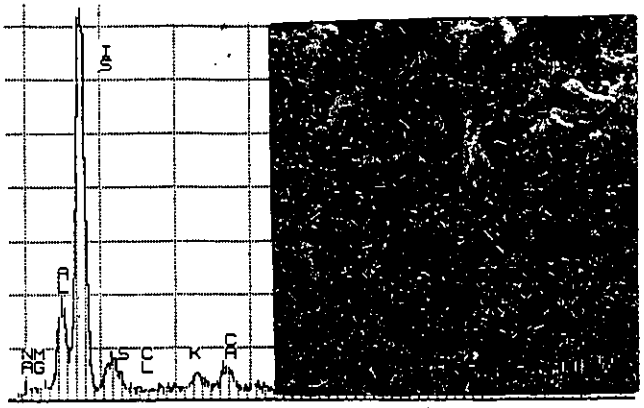
Fig. 4.5. XRD and SEM/EDXA analysis of H-HAC particulates after immersion in zeolite slurries containing different sodium salts.



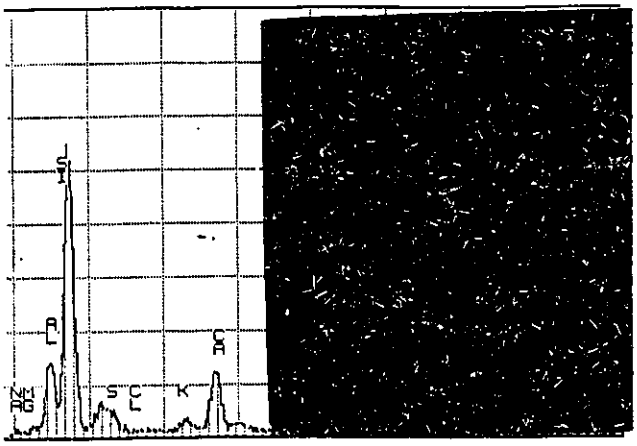
a. XRD Patterns



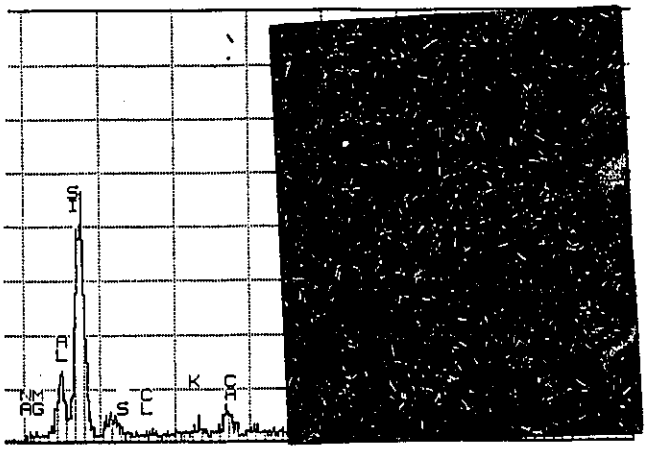
b. SEM/EDXA - effect of sodium silicate.



c. SEM/EDXA - effect of sodium carbonate.



d. SEM/EDXA - effect of sodium sulfate.



e. SEM/EDXA - effect of sodium nitrate.

Fig. 4.6. XRD and SEM/EDXA analysis of zeolite slurries containing H-HAC particulates and different sodium salts.

§ 4.4. Discussion

Strätlingite appears to grow preferentially on hydrated HAC particles rather than silica-bearing material, e.g. zeolite particles. The dissolved silicate concentration is relatively high in zeolite slurries containing H-HAC particulates (mainly consisting of CAH_{10}) and highly basic sodium salts, i.e. sodium silicate and sodium carbonate. Plate-like strätlingite crystals grow on the surface of H-HAC particulates. The dissolved silicate concentration is low in the HAC slurries containing zeolite particulates and different sodium salts. This is attributed to the lower surface area of the zeolite particulates (1.168-3.327 mm in diameter); strätlingite is still formed and uniformly distributed in the HAC slurries. This phenomenon indicates that the reactions associated with strätlingite formation may take place topochemically on the surfaces of the H-HAC particulates. Dissolution of calcium aluminate phases appears to be more difficult than for zeolite. Zeolite releases silicate ions to the solution when activated by sodium ions. The dissolved silica then reacts with the calcium aluminate phase on the surface of the H-HAC particulates. Re-crystallization of the calcium aluminate phase occurs in presence of sufficient silicate anions to form strätlingite. A relatively high pH environment, e.g. that resulting from addition of highly basic salts such as sodium silicate or sodium carbonate, appears to be more favorable for strätlingite formation. A lower pH environment appears to favor stellerite ($2CaO{\cdot}2Al_2O_3{\cdot}14SiO_2{\cdot}14H_2O$) formation instead of strätlingite. The basicity of stellerite is lower than strätlingite since it contains more silica-groups and relatively less calcium oxide. This phase may not exist in real HAC products as it requires a relatively low pH condition.

The H-HAC particulates were made by hydrating HAC paste at 0 °C. The hydration product was mainly CAH_{10}. CAH_{10} usually converts to C_2AH_8 at room temperature and to C_3AH_6 at elevated temperature as it is thermodynamically unstable.

Test results indicate that the stability of CAH_{10} increases at low pH and high microsilica content. Reactions to form strätlingite or stellerite are believed to take place only in the out layer of the H-HAC particulates. The core of the H-HAC particulates remains unchanged after 2 months curing at room temperature. It is in the form of CAH_{10}.

§ 4.5. Conclusions

1. Strätlingite appears to grow preferentially on hydrated HAC particles rather than on silica-bearing particles.

2. A sufficiently high silicate concentration and pH environment is required for strätlingite formation in HAC paste.

3. The thermodynamic stability of CAH_{10} is apparently increased at high microsilica content.

Chapter 5

CONVERSION-PREVENTING ADDITIVES FOR HIGH ALUMINA CEMENT PRODUCTS

- Effect of Different Inorganic Chemicals
- Effect of Different Pozzolans
- Effect of Different Zeolites

§ 5.1. Introduction

High alumina cement (HAC) was developed at the beginning of this century as part of efforts to develop alternative to Portland cement. HAC finds many specialized industrial applications by virtue of its rapid hardening and good resistance to chemical attack. The annual production of HAC is, however, only a small fraction of that of Portland cement due to the so-called "conversion" process.

A number of studies have investigated alternative reaction paths for the hexagonal aluminates to overcome the strength reduction due to the conversion process. One successful approach was achieved through the use of ground granulated blast furnace slag (ggbs). A replacement of 30% was found to be effective at the BRE (Building Research Establishment,UK). The one-day strength was however significantly lower than for the plain HAC concrete. The hydration reaction involved in the HAC/ggbs system is associated with strätlingite formation. The use of silica fume in combination with sodium tripolyphosphate as a defloculating agent in the HAC mortars was reported by Marcdargent et al. The strength reduction of such mortars, water-cured at 38 °C, was also restricted when w/c=0.3 was employed. The significant role of alkali ions on strätlingite formation in the HAC-microsilica system was reported in chapter 3. A new conversion-preventing additive comprised of alkali salts and silica based materials has been recently developed by the candidate. The one-day compressive strength of HAC mortars containing 10-30% additive, with a water/solid (HAC + additive) ratio of 0.40, was as high as 60 MPa. The modified HAC products undergo no strength reduction at later ages when water-cured at 38 °C. A large amount of strätlingite was formed in the products.

The research described in this chapter is aimed at demonstrating the effect of different inorganic chemicals on conversion reactions that form strätlingite and

hydrogarnet in HAC/zeolite blended cement systems. The effect of different pozzolans and the effect of different zeolites was also determined.

§ 5.2. Effect of different inorganic chemicals

§ 5.2.1. Experimental

§ 5.2.1.1. Materials

- High alumina cement (HAC): Ciment Fondu, produced by Lafarge Calcium Aluminates, Virginia, USA, was used;
- Natural zeolite-A: containing mainly clinoptilolite and gismondine, supplied by Polar Powder Technologies, Inc., Alberta, Canada;
- Natural zeolite-B: containing mainly clinoptilolite, levyne and offretite, supplied by Zeotech Corporation, New Mexico, USA.
- Reagent grade salts used included: sodium sulfate, sodium carbonate, sodium nitrate, sodium chloride, sodium bromide, sodium metaphosphate, sodium metasilicate, sodium hydroxide, potassium hydroxide, lithium chloride, potassium carbonate, copper sulfate, aluminum sulfate.

The oxide compositions of HAC, zeolite A and zeolite B are listed in Table 5.1.

Table 5.1. Oxide Composition (% by mass) of Selected Natural Zeolites

Oxides (% by mass)	HAC	Natural Zeolite A	Natural Zeolite B
SiO_2	4.5	65.8	65.7
Al_2O_3	41.2	14.3	12.5
CaO	39.8	3.4	2.0
Fe_2O_3	11.3	2.6	1.7
MgO	0.6	1.3	0.9
Na_2O	0.1	2.5	1.5
K_2O	-	2.7	1.7
MnO	-	0.04	0.9

§ 5.2.1.2. Test methods and analysis

Compressive Strength: Cement mortars were prepared for determination of compressive strength. Natural zeolite-A was used in this test. The sand/HAC ratio was 2.75 and the water/solid (HAC + zeolite) ratio was 0.40. Composition of the specimens is given in Table 5.2. The cement mortar was mixed for 3 minutes and then cast in 50.8x50.8x50.8 mm cube moulds. The specimens were demoulded after 24 hours moist-curing at 23 °C. The one-day compressive strength was determined immediately after demoulding. Companion specimens were placed in water at 38 °C to continue hydration.

Table 5.2. Composition of HAC/Zeolite Mortars Containing Different Inorganic Additives

Samples	Zeolite-A (wt. % of HAC)	Sodium Salts Anions	Sodium Salts Content (wt.% of HAC)
1	-	-	-
2	20.0	-	-
3	20.0	Sulfate	1.0
4	20.0	Silicate	1.0
5	20.0	Phosphate	1.5
6	14.5	Carbonate	1.5
7	20.0	Nitrate	2.0

X-ray diffraction analysis: The composition of HAC pastes prepared for x-ray diffraction analysis is provided in Table 5.3. Natural zeolite-B was used in this test. Samples 1 to 5 and 8 to 10 had the same alkali oxide (M_2O) content, i.e. $3.4x10^{-4}$ mol M_2O per gram of HAC. These samples were intended to demonstrate the effect of alkali ions. Samples 1, 12 and 13 had the same sulfate content, i.e. $3.4x10^{-4}$ mol $SO_4^=$ per gram of HAC. These samples were used to demonstrate the effect of sulfate ions in presence of different cations. Since sodium metaphosphate and sodium metasilicate significantly retarded the hardening of HAC paste, the amount added was less than for the other salts. The cement paste samples were prepared with a water/solid (HAC+zeolite) ratio = 0.60. The paste samples were cast in 25 mm diameter bottles and rotated for 24 hours at 38 °C. Samples were water-cured at 38 °C after demoulding. X-ray diffraction analysis was

carried out on wet samples after grinding in an agate mortar. The test was designed for the comparison of parallel samples prepared by identical process. The comparison is based on significant differences between parallel samples. Some samples were repeated three times. The relative error of peak height (e.g. C_2ASH_8 at d=1.07 nm, calculated by Rigaku Standard Data Processing software) was 10%. A Rigaku X-ray Diffractometer System Geigerflex D/Max -B was used for the x-ray studies.

Table 5.3. Composition of HAC/Zeolite Pastes Used in XRD Analysis (arbitrary mass units)

			Inorganic Chemicals Additive	
Samples	HAC	Zeolite-B	Type	content
1	1	0.2	Sodium sulfate	0.048
2	1	0.2	Sodium carbonate	0.036
3	1	0.2	Sodium nitrate	0.057
4	1	0.2	Sodium chloride	0.040
5	1	0.2	Sodium bromide	0.069
6	1	0.2	Sodium metaphosphate	0.010
7	1	0.2	Sodium metasilicate	0.050
8	1	0.2	Potassium carbonate	0.047
9	1	0.2	Lithium chloride	0.028
10	1	0.2	Sodium hydroxide	0.028
11	1	0.2	Potassium hydroxide	0.038
12	1	0.2	Copper sulfate ($CuSO_4 \cdot 5H_2O$)	0.085
13	1	0.2	Aluminum sulfate* ($Al_2(SO_4)_3 \cdot 14\text{-}18H_2O$)	0.071

*Dosage of aluminum sulfate is based on the formula $Al_2(SO_4)_3 \cdot 16H_2O$.

§ 5.2.2. Results and discussion

The effect of different sodium salts on strength development of HAC/zeolite mortars is shown in Table 5.4. The one-day strength was obtained from the specimens moist-cured at 23 °C. The companion specimens were then placed in water at 38 °C. The plain HAC mortar had the highest compressive strength (65 MPa) at one day. Its strength decreased dramatically to 34 MPa at 14 days due to the conversion reaction. The strength

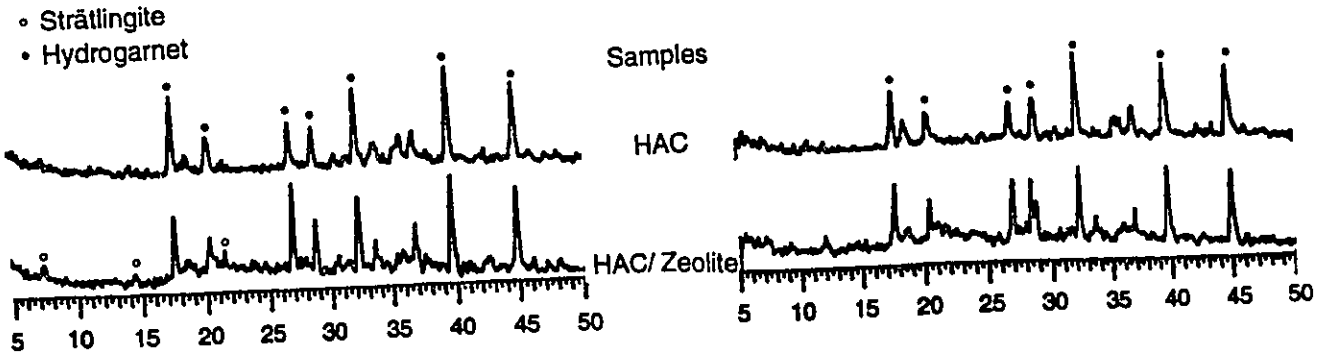
Table 5.4. Compressive Strength of HAC/Zeolite Mortars

Samples	Composition			Compressive Strength (MPa)			
	Zeolite-A (wt. of HAC)	Anions of Sodium Salts	Sodium Salts Content (wt. % of HAC)	1 Day#	14 Days*	28 Days*	150 Days*
1	-	-	-	65	34	36	34
2	20.0	-	-	57	38	40	45
3	20.0	Sulfate	1.0	62	65	69	72
4	20.0	Silicate	1.0	29	35	41	57
5	20.0	Phosphate	1.5	30	38	45	59
6	14.5	Carbonate	1.5	40	53	57	57
7	20.0	Nitrate	2.0	34	50	52	63

 # - moist-cured at 23 °C;
** - water-cured at 38 °C after the first 24 hours moist-curing at 23 °C.*

remained at this level up to 150 days. The HAC mortar containing zeolite alone had a lower one-day strength value than the plain HAC mortar. Strength reduction still occurred in this sample. Its 14-day strength was slightly higher than that of the plain HAC mortar. Little strength recovery occurred. The strength increased from 38 MPa at 14 days to 45 MPa at 150 days. Addition of sodium sulfate resulted in a high one-day strength (62 MPa). The strength increased to 69 MPa at 28 days and 72 at 150 days. Sodium metasilicate and sodium phosphate significantly retarded the HAC hydration. They resulted in a low one-day strength (about 30 MPa) in the HAC/zeolite mortar. The strength then increased with age. The specimens had an increase in strength of about 40% from 1 to 28 days and a further 40% increase at 150 days. Sodium carbonate and sodium nitrate addition also resulted in a relatively low one-day strength. They however exhibited a very high rate of strength gain in the first 14 days. The 14-day compressive strength values of the HAC/zeolite mortars containing either of these two salts were all above 50 MPa. Strength continuously increased until 150 days. It is apparent that no strength reduction due to curing at elevated temperature occurred in the HAC/zeolite mortars containing one of the sodium salts.

The x-ray diffraction (XRD) spectra of plain HAC paste and HAC/zeolite paste are shown in Fig. 5.1. Hydrogarnet (C_3AH_6) formed in both plain HAC and HAC/zeolite pastes at all ages. Little difference in hydrogarnet peaks could be found between the plain HAC and the HAC/zeolite pastes. Strätlingite were detected. Zeolite alone could not prevent the hydrogarnet formation in HAC paste.

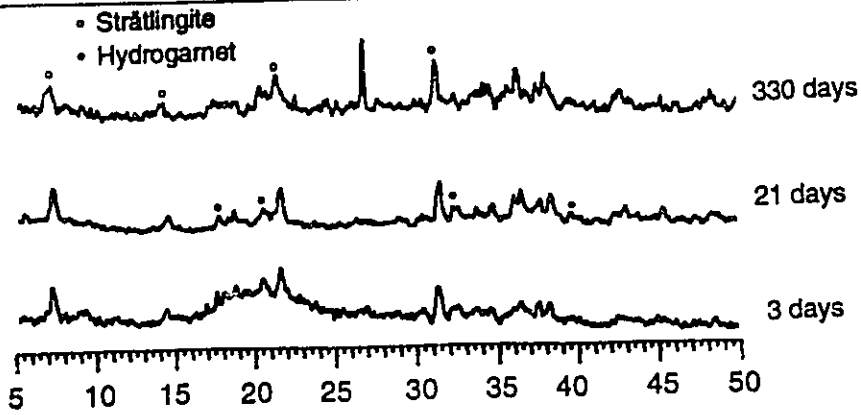


Degrees (2θ) Degrees (2θ)

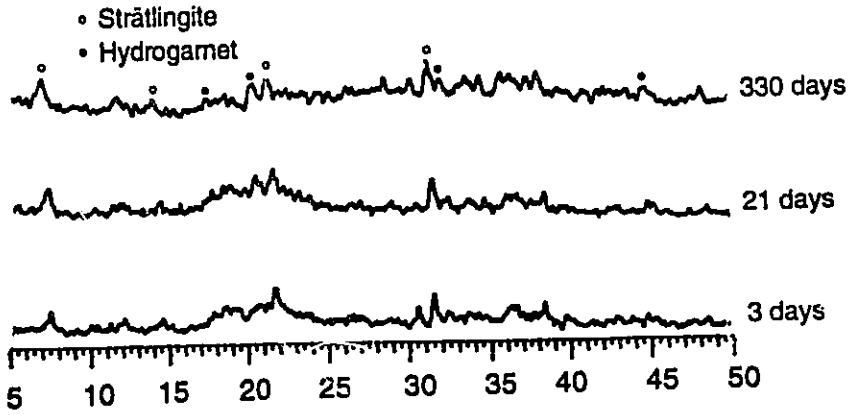
(a) 7 days (b) 330 days

Fig. 5.1. XRD spectra of plain HAC paste and the HAC/zeolite paste.

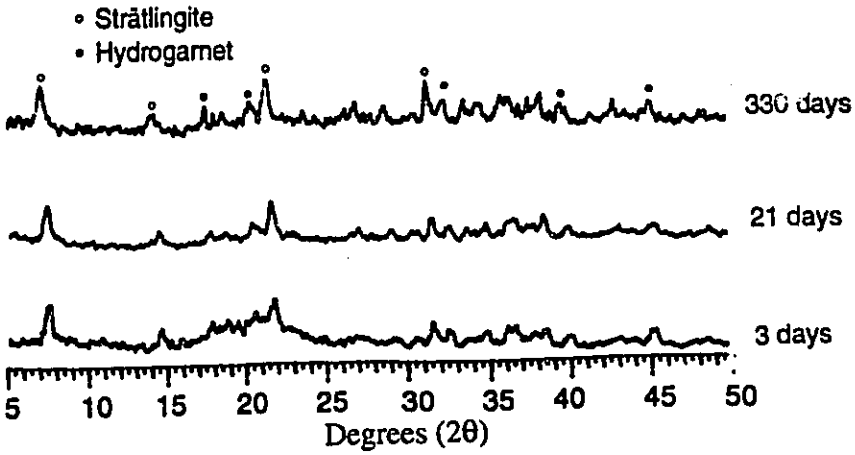
The XRD spectra of the HAC/zeolite pastes containing different sodium oxy-acids, e.g. Na_2SO_4, Na_2CO_3 and Na_2NO_3, are shown in Fig. 5.2. Strätlingite formation was apparently promoted in the HAC/zeolite pastes by the addition of sodium oxy-acids. The strätlingite peaks at 3 days was similar to that at 330 days. Strätlingite formed at very early ages. Only very small peaks of hydrogarnet were detected. Hydrogarnet formation was apparently inhibited in these systems.



(a) Effect of sodium sulfate



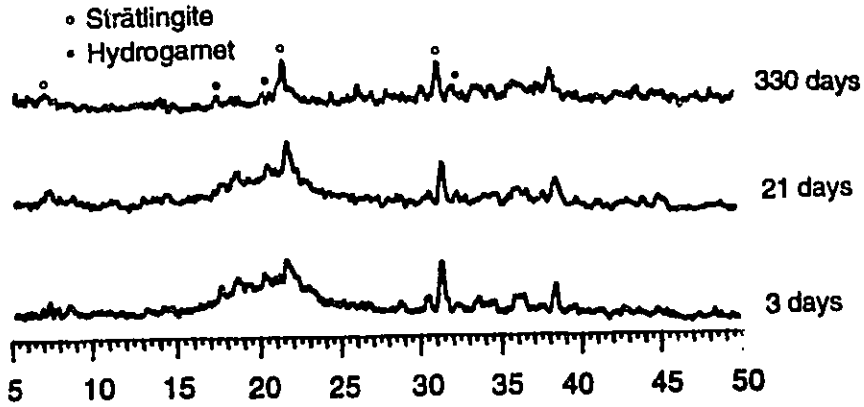
(b) Effect of sodium carbonate



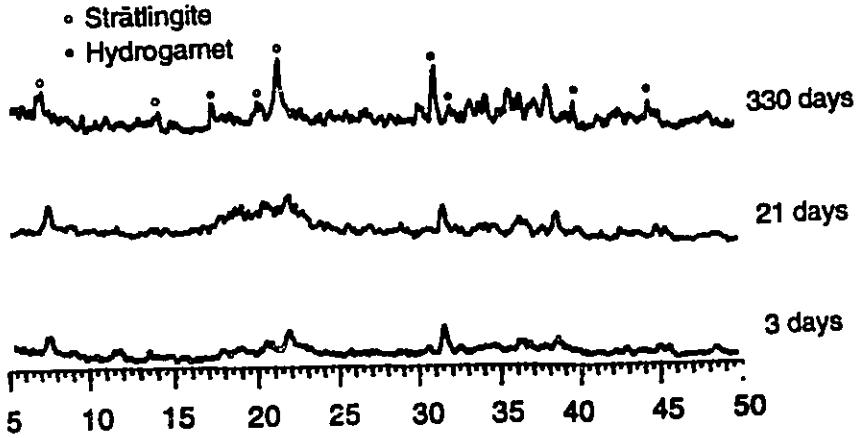
(c) Effect of sodium nitrate

Fig. 5.2. XRD spectra of the HAC/zeolite pastes containing sodium oxy-acids.

The XRD spectra of the HAC/zeolite pastes containing different sodium halogenides, e.g. NaCl and NaBr, are shown in Fig. 5.3. Strätlingite formed in the sample containing sodium chloride and sodium bromide at all ages. The strätlingite peak at d=1.258 nm in the sample containing sodium bromide was very small; its peaks at d=0.418 and 0.287 nm were relatively high. Preferred orientation of strätlingite crystals may differ in presence of different halogenides. Little hydrogarnet was detected in samples containing the sodium halogenides.



(a) Effect of sodium chloride.

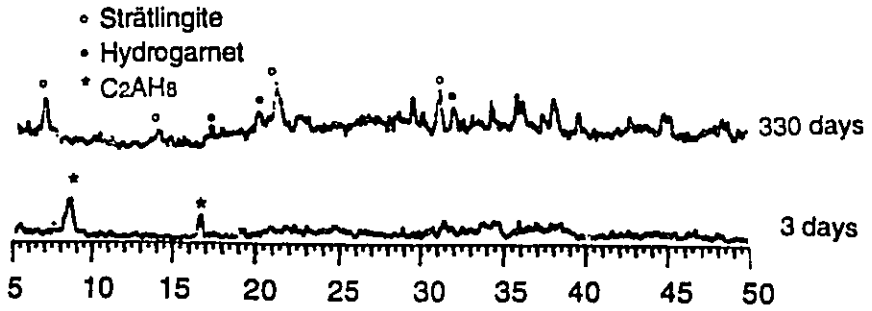


(b) Effect of sodium bromide.

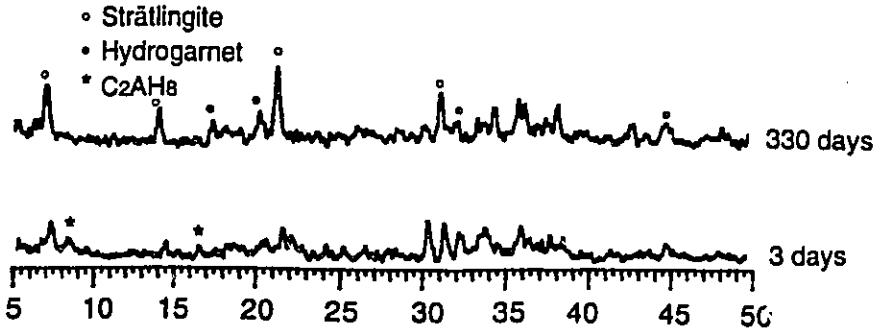
Fig. 5-3. XRD spectra of the HAC/zeolite pastes containing sodium halogenides.

The XRD spectra of the HAC/zeolite pastes containing sodium metaphosphate or sodium metasilicate are shown in Fig. 5.4. Sodium phosphate has been found to accelerate the setting time but to retard the hardening of HAC paste. Strätlingite formation was delayed in the sample containing sodium metaphosphate. Strätlingite was not detected at 3 days. Distinct peaks of strätlingite appeared at 330 days. C_2AH_8 existed in the sample at 3 days and eventually converted to strätlingite, It appears that sodium metaphosphate can stabilize the hexagonal aluminate phase formed at high humidities and 38 °C. This was in agreement with the results reported by Marcdargent et al [12]. Sodium metasilicate apparently promoted strätlingite formation in the HAC/zeolite system. Relatively large peaks attributed to strätlingite were recorded at 3 days. C_2AH_8 was also found in the sample at 3 days when water-cured at 38 °C. Little hydrogarnet was detected in the samples containing sodium metaphosphate or sodium metasilicate.

The XRD spectra of the HAC/zeolite pastes containing potassium carbonate and lithium chloride are shown in Fig. 5.5. Small strätlingite peaks were observed in the sample containing potassium carbonate. They were also detected in the sample containing lithium chloride. Hydrogarnet formed in both samples. The peak heights were greatly reduced compared to the plain HAC and the HAC/zeolite pastes (see Fig.5.1 having the same ordinate scale). It appears that sodium ions are probably more effective in preventing the formation of hydrogarnet than the other alkali ions, e.g. potassium or lithium. Potassium ions had little effect in promoting strätlingite formation. Lithium ions did not appear to promote strätlingite formation.

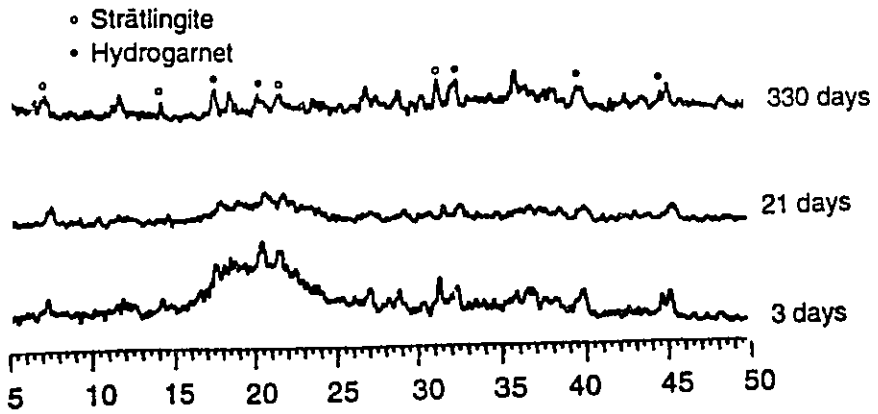


Degrees (2θ)
(a) Effect of sodium metaphosphate

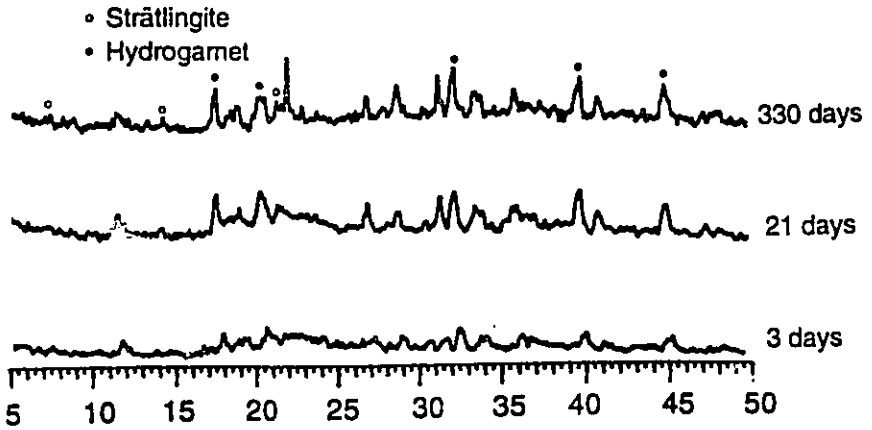


Degrees (2θ)
(b) Effect of sodium metasilicate

Fig. 5.4. XRD spectra of the HAC/zeolite pastes containing sodium metaphosphate or sodium metasilicate.



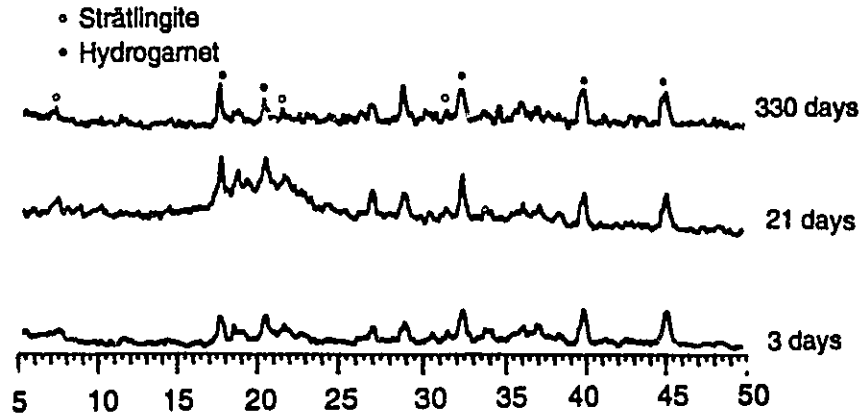
Degrees (2θ)
(a) Effect of potassium carbonate.



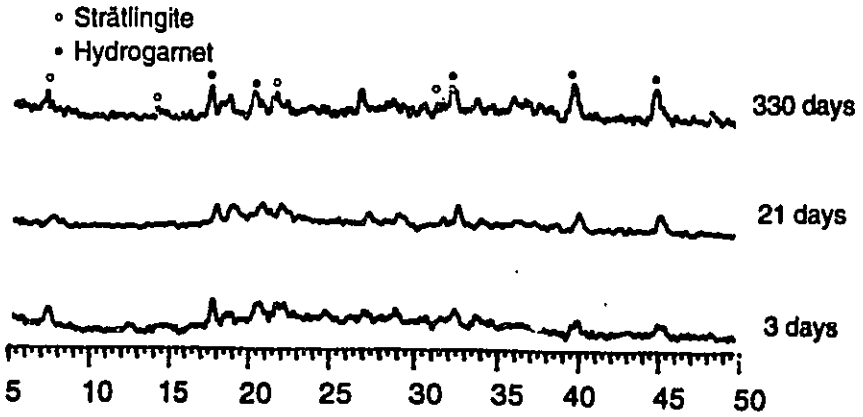
Degrees (2θ)
(b) Effect of lithium chloride.

Fig. 5.5. XRD spectra of the HAC/zeolite pastes containing potassium carbonate or lithium chloride.

The XRD spectra of the HAC/zeolite pastes containing NaOH and KOH are shown in Fig. 5.6. Addition of either NaOH or KOH to HAC paste results in rapid setting. Strätlingite formed in both samples. Hydrogarnet still formed in the samples containing alkali hydroxides. A very high pH condition appeared to favour the hydrogarnet formation.



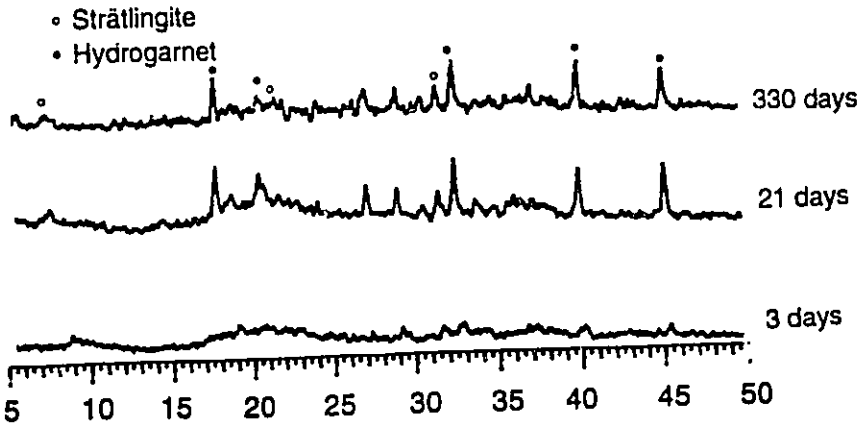
(a) Effect of sodium hydroxide.



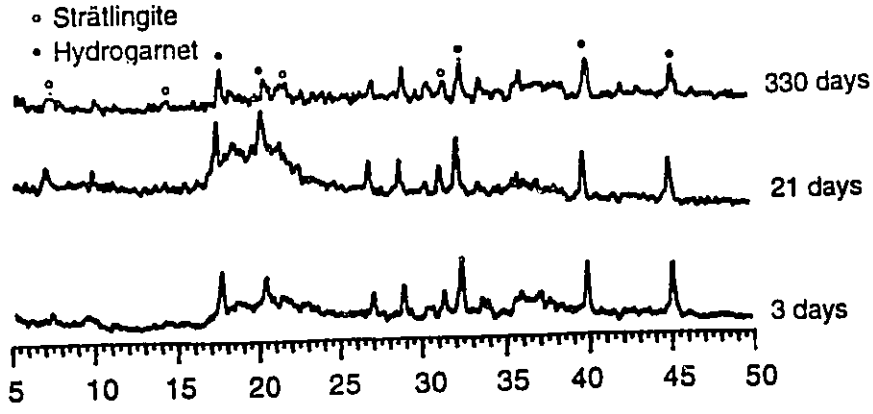
(b) Effect of potassium hydroxide.

Fig. 5.6. XRD spectra of the HAC/zeolite pastes containing sodium hydroxide or potassium hydroxide.

The XRD spectra of the HAC/zeolite pastes containing $CuSO_4 \cdot 5H_2O$ and $Al_2(SO_4)_3 \cdot 14\text{-}18H_2O$, are shown in Fig. 5.7. Relatively large peaks of hydrogarnet were observed. Sulfate appears not to affect the formation of strätlingite and hydrogarnet in HAC. Metal ions having a valence of 2 or 3 did not prevent hydrogarnet formation in HAC/zeolite products. These ions are apparently not able to activate the zeolite.



(a) Effect of copper sulfate.



(b) Effect of aluminum sulfate.

Fig. 5.7. XRD spectra of the HAC/zeolite pastes containing copper sulfate or aluminum sulfate.

The evidence described above supports the argument that sodium ions play a significant role in the reactions leading to strätlingite formation. It is apparent that the sodium ions can interact with silica and cause the pH value of the system to increase [12]. Silica reacts to form silicates in a high pH environment. This reaction is accelerated in presence of alkali ions. A sufficient amount of dissolved silicate anions then react with hydrated calcium aluminates (C_2AH_8 or CAH_{10}) to produce strätlingite in preference to hydrogarnet. Rao and Viswanathan have indicated that the timing of strätlingite formation is important in preventing strength retrogression in high alumina cements [3]. The presence of sodium ions facilitates the supply of sufficient dissolved silicate at early ages. Continuous release of silicate from added siliceous material to form strätlingite contributes to the strength gain property of improved high alumina cement products.

§ 5.2.3. Conclusions

1. The one-day compressive strength of the HAC/zeolite mortars containing a sodium salt (sodium sulfate, sodium carbonate, sodium nitrate, sodium metaphosphate and sodium metasilicate) is in the range of 30 to 60 MPa. No strength reduction occurs in these mortars water-cured at 38 °C for 150 days.

2. Strätlingite formation is apparently promoted and hydrogarnet formation is significantly inhibited, by the addition of sodium salts, e.g. sodium bromide, sodium carbonate, sodium nitrate, sodium chloride, sodium sulfate, sodium metaphosphate or sodium metasilicate, to the HAC/zeolite system.

3. The beneficial effects of the conversion-preventing additives utilized in this study are generally independent of anion type.

4. Additives containing metal ions with higher valences appear to have no effect on strätlingite and hydrogarnet formation in HAC/zeolite systems.

§ 5.3. Effect of different pozzolans

§ 5.3.1. Experimental

§ 5.3.1.1. Materials

The following materials were used in this study:

- High alumina cement (HAC), Ciment Fondu, produced by Lafarge Calcium Aluminates, Virginia, USA;
- Natural zeolite, containing mainly clinoptilolite and gismondine, supplied by Polar Powder Technologies, Inc., Alberta, Canada;
- Silica fume (SF), supplied by the SKW Co., Montreal, Canada;
- ASTM class F fly ash (FA-F);
- ASTM class C fly ash (FA-C);
- Sodium sulfate, reagent grade.

The oxide analysis of HAC and pozzolans are listed in Table 5.5.

Table 5.5. Oxide Compositions of HAC and Pozzolans

	Oxide Compositions (mass %)						
	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O+K_2O	SO_3
HAC	4.5	31.2	39.8	11.3	0.60	0.10	-
Zeolite	65.8	14.3	3.4	2.6	1.3	5.2	-
SF	95.2	0.2	0.2	0.1	0.2	0.4	0.1
FA-F	53.1	25.9	12.3	3.5	1.3	2.4	0.2
FA-C	37.2	20.1	23.0	6.5	5.8	1.7	1.3

§ 5.3.1.2. Test methods and analysis

Compressive Strength Test: Cement mortars were prepared for determination of compressive strength. The sand/HAC ratio was 2.75 and the water/solid (HAC + pozzolan) ratio was 0.40. The cement mortar was mixed for 3 minutes and then cast in 50.8x50.8x50.8 mm cube moulds. The specimens were demoulded after 24 hours moist-curing at 23 °C. The one-day compressive strength was determined after demoulding. Companion specimens were placed in water at 38 °C after demoulding. The composition of the HAC/Pozzolan Mortars is given in Table 5.6.

Table 5.6. Composition of HAC/Pozzolan Mortars Containing a Sodium Sulfate

Samples	Sodium Sulfate (mass. % of HAC)	Pozzolan Type	Pozzolan Content (mass.% of HAC)
-	-		-
-	-		-
M-2	1.0	Zeolite	20.0
M-3	2.0	SF	20.0
M-4	2.0	FA-C	20.0
M-5	2.0	FA-F	20.0

X-ray diffraction analysis: Composition of the HAC pastes prepared for x-ray diffraction analysis is given in Table 5.7. The cement paste samples were prepared with a water/solid (HAC + pozzolans) ratio = 0.60. The paste samples were cast in 25 mm diameter bottles and rotated for 24 hours at 38 °C. Samples were water-cured at 38 °C after demoulding. X-ray diffraction analysis was carried out on wet samples after grinding in an agate mortar. The test was designed for the comparison of parallel samples prepared by identical process. The comparison is based on significant differences between parallel samples. Some samples were repeated three times. The relative error of peak height (e.g. C_2ASH_8 at d=1.07 nm, calculated by Rigaku Standard Data Processing

software) was 10%. A Rigaku X-ray Diffractometer System Geigerflex D/Max -B was used for x-ray studies.

Table 5.7. Composition of HAC/Pozzolan Pastes (arbitrary mass units)

Samples	HAC	Na_2SO_4	Siliceous Materials Type	content
1	1	-	-	-
2	1	0.047	-	-
3	1	-	Zeolite	0.3
4	1	0.047	Zeolite	0.3
5	1	-	Silica fume	0.3
6	1	0.047	Silica fume	0.3
7	1	-	Class C fly ash	0.3
8	1	0.047	Class C fly ash	0.3
9	1	-	Class F fly ash	0.5
10	1	0.047	Class F fly ash	0.5

§ 5.3.2. Results and discussion

The effect of different pozzolans on strength development of HAC/pozzolan mortars is shown in Table 5.8.

Table 5.8. Compressive Strength of HAC Mortars

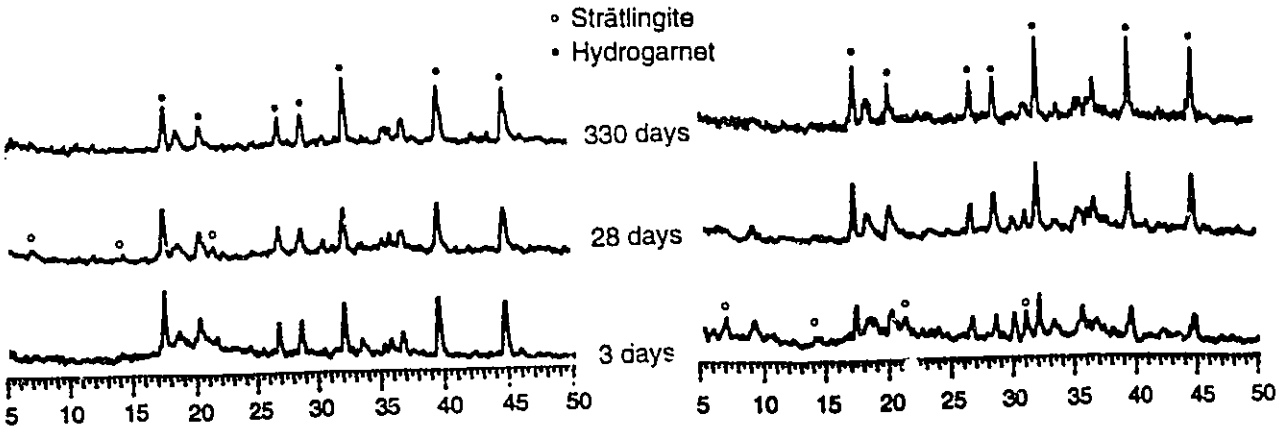
Samples	1 day#	14 days*	28 days*	150 days*	330 days*
M-1	65	34	36	34	34
M-2	62	65	69	72	72
M-3	29	52	62	66	69
M-4	32	37	44	67	72
M-5	39	42	44	55	56

 # - moist-cured at 23 °C;
** - water-cured at 38 °C after the first 24 hours moist-curing at 23 °C.*

The one-day strength was obtained for specimens moist-cured at 23 °C. Companion specimens were then placed in water at 38 °C. The plain HAC mortar had the highest compressive strength (65 MPa) at one day. Its strength decreased dramatically to 34 MPa at 14 days due to the conversion reaction. The strength then remained at this level up to 330 days. The HAC mortar containing a pozzolan and sodium sulfate had a lower one-day strength than the plain HAC mortar when moist-cured at 23 °C. The HAC/zeolite

mortar had a much higher one-day compressive strength value (62 MPa) than the other mortars containing a pozzolan. Strength increased continuously to 72 MPa at 330 days. The HAC mortar containing silica fume and sodium sulfate had a very low one-day compressive strength value (29 MPa). The strength increased greatly to 52 MPa at 14 days and exceeded 60 MPa at 28 days. The one-day strength of the HAC mortar containing fly ash and sodium sulfate was higher than the HAC/SF mortar. The early strength of the class F fly ash (FA-F) mortar exceeded that of the class C fly ash (FA-C). The long term strength of the HAC/FA-F mortar however was significantly lower than that of the HAC/FA-C mortar. The 330-day strength of the HAC mortar containing FA-C and FA-F was 72 and 56 MPa respectively. The strength reduction of the HAC mortar was prevented by the addition of a pozzolan in combination with sodium sulfate. Strength increased continuously with age.

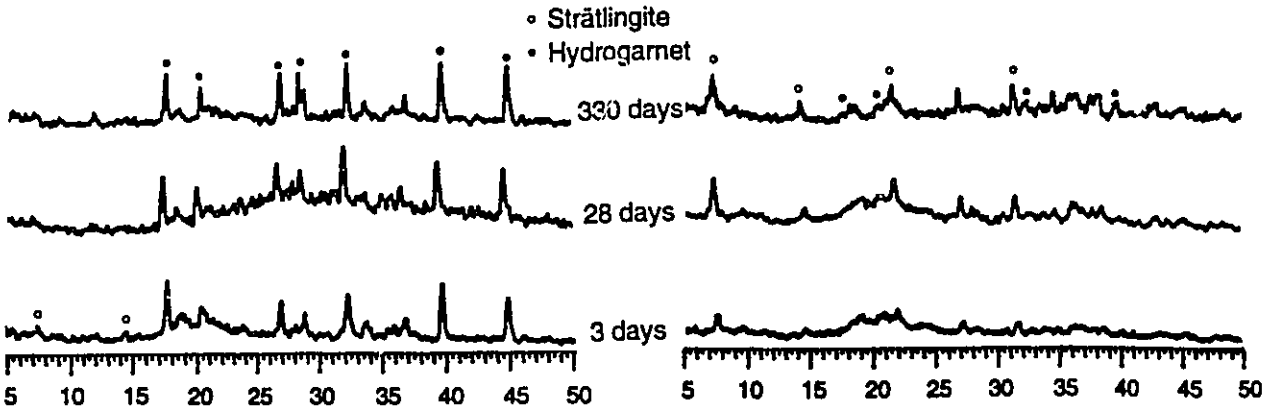
The x-ray diffraction (XRD) spectra of plain HAC paste and HAC paste containing 4.7% sodium sulfate by mass of HAC are shown in Fig. 5.8. Hydrogarnet (C_3AH_6) formed in both plain HAC and HAC/sodium sulfate pastes at all ages. The peak intensities of hydrogarnet in the HAC/zeolite paste (Fig.5.9.) were smaller than those in the plain HAC paste at 3 days (Fig. 5.8a), indicating that sodium sulfate could temporarily suppress the formation of hydrogarnet at early ages. Small peaks representing strätlingite were detected in the sample containing sodium sulfate at 3 days (Fig. 5.8b). These peaks were disappeared after 28 days. Sodium sulfate appeared to accelerate strätlingite formation at 38 °C and at early ages. The reason for the disappearance of strätlingite in the HAC - sodium sulfate system at later ages is not clear. Sodium sulfate alone is not able to inhibit the hydrogarnet formation.



Degrees (2θ) Degrees (2θ)

(a) Plain HAC (b) HAC/sodium sulfate

Fig. 5.8. XRD spectra of a plain HAC paste and an HAC paste containing sodium sulfate.



Degrees (2θ) Degrees (2θ)

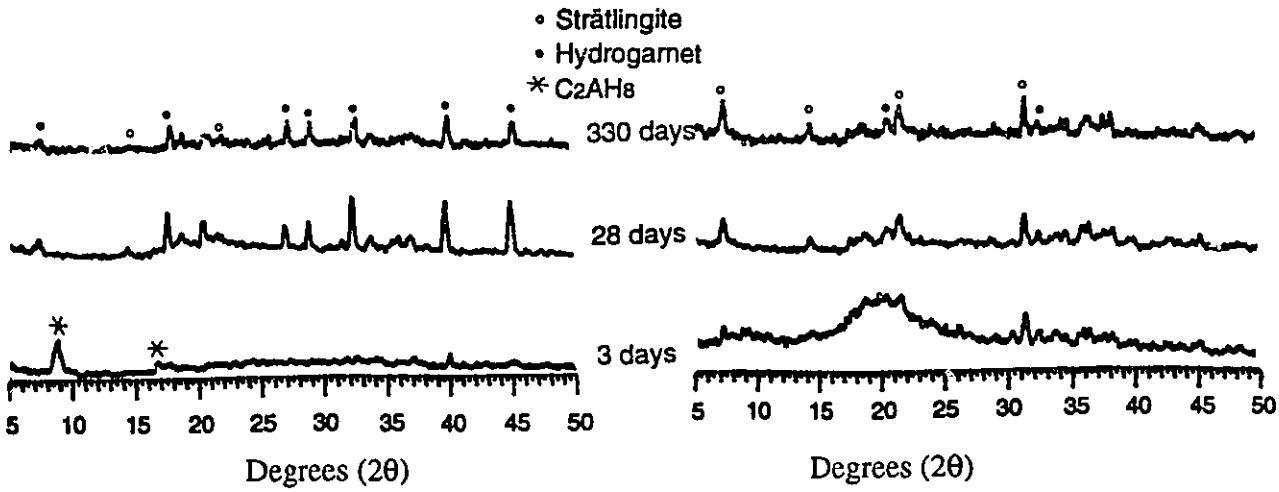
(a) HAC/zeolite (b) HAC/zeolite+sodium sulfate

Fig. 5.9. XRD spectra of an HAC/zeolite paste and an HAC/zeolite paste containing sodium sulfate.

The XRD spectra of an HAC paste containing 30% zeolite and an HAC paste containing 30% zeolite and 4.7% sodium sulfate, by mass of HAC, are shown in Fig. 5.9.

Hydrogarnet peaks were recorded in the HAC/zeolite paste at 3 days (Fig. 5.9a). Strätlingite was detected at all ages. Little or no hydrogarnet was found in the HAC/zeolite paste containing sodium sulfate at 3 and 28 days (Fig. 5.9b). Very small hydrogarnet peaks were detected at 330 days. Strätlingite apparently formed at 3 days. Its peak intensity increased at 28 days and then remained unchanged.

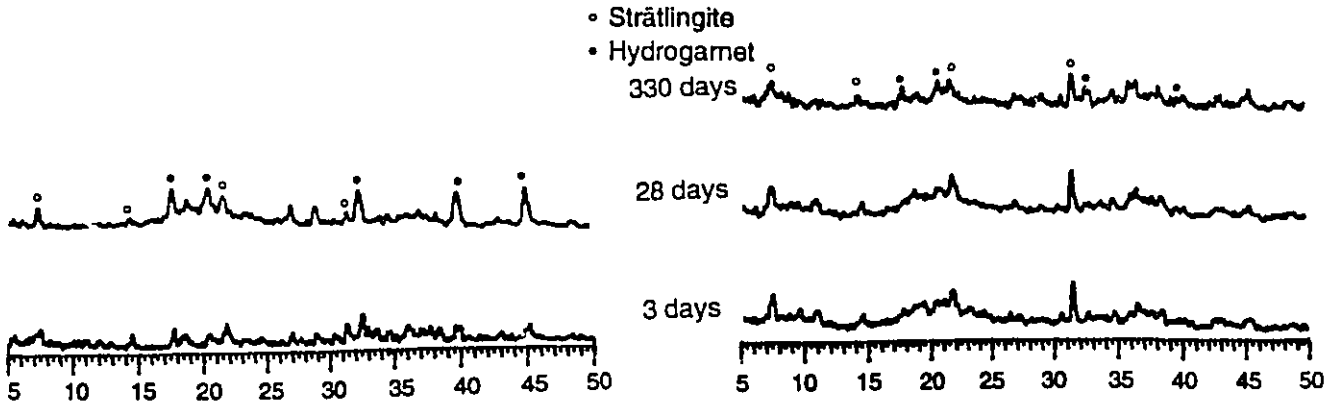
The XRD spectra of an HAC paste containing 30% silica fume (SF) and an HAC paste containing 30% SF and 4.7% sodium sulfate, by mass of HAC, are shown in Fig.5.10. A strong peak at d=1.07 nm was found representing the C_2AH_8 phase in the HAC/SF paste at 3 days (Fig. 5.10a). Hydrogarnet and strätlingite were detected at 28 days. Little or no hydrogarnet formed in the HAC/SF paste containing sodium sulfate (Fig. 5.10b). The Strätlingite peaks increased steadily with age. A hump around 2θ=20° occurred at 3 days and disappeared at 28 days. It is suggested that this hump might represent the reaction products of silica fume activated by sodium ions in the system.



(a) HAC/silica fume (b) HAC/silica fume + sodium sulfate

Fig. 5.10. XRD spectra of an HAC/silica fume paste and an HAC/silica fume paste containing sodium sulfate.

The XRD spectra of an HAC paste containing 30% Class C fly ash (FA-C) and an HAC paste containing 30% FA-C and 4.7% sodium sulfate, by mass of HAC, are shown in Fig.5.11. Hydrogarnet begins to form in the HAC/FA-C paste at 3 days (Fig. 5.11a). Several hydrogarnet peaks were observed at 28 days. Strätlingite was detected at early ages. Little or no hydrogarnet was found in the HAC/FA-C paste containing sodium sulfate (Fig. 5.11b).



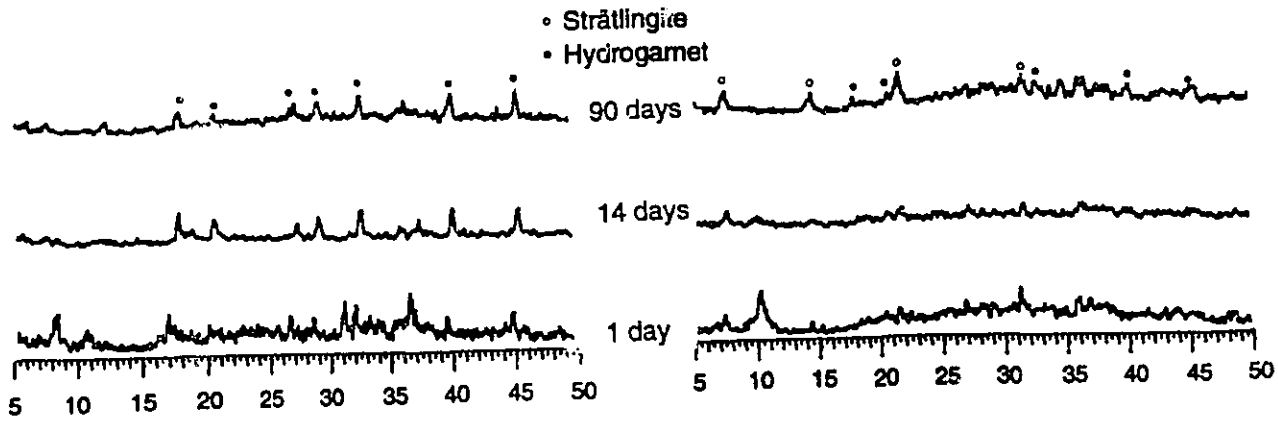
Degrees (2θ) Degrees (2θ)

(a) HAC/class C fly ash (b) HAC/class C fly ash + sodium sulfate

Fig. 5.11. XRD spectra of an HAC/FA-C paste and an HAC/FA-C paste containing sodium sulfate

The XRD spectra of an HAC paste containing 50% Class F fly ash (FA-F) and an HAC paste containing 50% FA-F and 4.7% sodium sulfate, by mass of HAC, are shown in Fig.5.12. Hydrogarnet was detected at 1 day in the HAC/FA-F paste (Fig. 5.12a). Little or no strätlingite was detectable in the HAC/FA-F paste. C_2AH_8 existed in the paste at 1 day and disappeared at 14 days. Little or no hydrogarnet was found in the HAC/FA-F paste containing sodium sulfate before 14 days (Fig. 5.12b). Small peaks of hydrogarnet appeared in the paste at 90 days. Strätlingite peaks were detected at 1 day

and increased with age. It is clearly shown that strätlingite formation was accelerated and hydrogarnet inhibited, by the addition of sodium sulfate in the HAC/fly ash paste.



(a) HAC/class F fly ash (b) HAC/class F fly ash + sodium sulfate

Fig. 5.12. XRD spectra of an HAC/FA-F paste and an HAC/FA-F paste containing sodium sulfate.

Hydration of high alumina cement blended with various siliceous materials has been intensively studied by Majumdar et al.[7] and Bentsen et al [9]. The use of siliceous materials alone in HAC to effectively prevent strength reduction due to conversion required very high dosages up to 100% by mass of the HAC. It is apparent that the inhibition of the conversion of CAH_{10} or C_2AH_8 to C_3AH_6 depends on the amount and rate of dissolved silica released from the siliceous materials added. The slow reaction rate of silica fume in HAC paste has been reported [11]. Increase addition of siliceous materials promotes strätlingite formation. Sodium salts act as an activator to accelerate the reaction of siliceous materials in the HAC system. Silica dissolves to silicate anions more quickly in presence of sodium ions. The silicate anions then react with the hexagonal calcium aluminate hydrates to form strätlingite in preference to hydrogarnet. This reaction prevents the strength reduction. A relatively low content of siliceous

materials can be effective in preventing strength reduction in HAC products since more dissolved silicates can be supplied in presence of sodium ions.

§ 5.3.3. Conclusions

1. The one-day compressive strength of high alumina cement (HAC) mortars containing a pozzolan and sodium sulfate, with water/solid ratio 0.4, can be up to 60 MPa - a value nearly equivalent to that for unmodified HAC mortars.

2. No strength reduction occurs in high alumina cement mortars containing pozzolan and sodium sulfate subsequent to water-curing at 38 °C for 330 days. Compressive strength increases continuously with age.

3. Little or no hydrogarnet (C_2AH_6) forms in high alumina cement pastes containing pozzolans and sodium sulfate after water-curing at 38 °C for 330 days. Strätlingite (C_2ASH_8) formation is promoted in the pastes.

§ 5.4. Effect of different zeolites

§ 5.4.1. Experimental

§ 5.4.1.1. Materials

- High alumina cement (HAC): Ciment Fondu, produced by Lafarge Calcium Aluminates, Virginia, USA.;
- Zeolite-A: a natural mineral is from Texas, USA, containing mainly clinoptilolite, $(Na_4,K_4)Al_8Si_{40}O_{96}\cdot 24H_2O$, supplied by Zeotech Corporation, New Mexico, USA;
- Zeolite-B: a natural mineral is from Nevada, USA; containing mainly clinoptilolite and gismondine, supplied by American Resource Corporation, Inc., California, USA;

- Zeolite-C: a natural mineral is from Western Canada, containing mainly clinoptilolite and gismondine, supplied by Polar Powder Technologies, Inc., Alberta, Canada;
- Zeolite-D: a natural mineral is from Washington, USA; containing mainly clinoptilolite, supplied by Polar Powder Technologies, Inc., Alberta, Canada;
- Zeolite-E: a natural mineral is from Western Canada, containing mainly clinoptilolite; supplied by Polar Powder Technologies, Inc., Alberta, Canada;
- Zeolite-F: a natural mineral is from Arizona, USA, containing mainly chabazite, $Ca_2Al_4Si_8O_{24}\cdot 12H_2O$, supplied by Union Carbide Co. (UOP), Arizona, USA;
- Zeolite-G, a natural mineral is from Nova Scotia, Canada, containing mainly stilbite, $NaCa_2Al_{15}Si_{13}O_{36}\cdot 14H_2O$, supplied by Ward's Natural Science Establishment, Inc., Ontario, Canada;
- Zeolite-H, a natural mineral is from Oregon, USA, containing mainly natrolite, $Na_2Al_2Si_3O_{10}\cdot 2H_2O$, supplied by Ward's Natural Science Establishment, Inc., Ontario, Canada;
- Zeolite-I: a molecular sieve (type 4A), supplied by Aldrich Chemical Company, Inc., Milwaukee, USA;
- Zeolite-J: a molecular sieve (type 13X), supplied by Aldrich Chemical Company, Inc., Milwaukee, USA;
- Sodium sulfate, a reagent grade chemical supplied by Aldrich Chemical Company, Inc., Milwaukee, USA.

The oxide analysis of HAC and some zeolites (clinoptilolite group) are listed in Table 5.9.

Table 5.9. Oxide Compositions of HAC and Zeolites

	Oxide Compositions (mass %)						
	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O+K_2O	MnO
HAC	4.5	41.2	39.8	11.3	0.60	0.10	-
Zeolite -A	65.8	14.3	3.4	2.6	1.3	5.2	0.9
Zeolite-B	69.1	11.9	0.7	0.7	0.4	7.3	4.9
Zeolite-C	65.7	12.5	2.0	1.7	0.9	3.2	0.04

§ 5.4.1.2. Test Methods and Analysis

Compressive Strength Test: Cement mortars were prepared for determination of compressive strength. Zeolites-A, B, C, D and E were used in this test. These zeolites , comprising mainly clinoptilolite, are all available for industrial use in North America. Clinoptilolite is the most plentiful natural zeolite mineral in the world. The other zeolites, e.g. Zeolites-F - J, may not be suitable for use as a construction material because of their relatively high cost or limited availability. The sand/HAC ratio was 2.75 and the water/solid (HAC + zeolite) ratio was 0.40. The cement mortar was mixed for 3 minutes and then cast in 50.8x50.8x50.8 mm cube moulds. The specimens were demoulded after 24 hours moist-curing at 23 °C. The one-day compressive strength value was determined after demoulding. Companion specimens were placed in water at 38 °C after demoulding. Composition of HAC/zeolite mortars is given in Table 5.10.

Table 5.10. Content of Additives and Compressive Strength Values of HAC/Zeolite Mortars Containing Sodium Sulfate

Samples	Sodium Sulfate (mass. % of HAC)	Zeolites Type	Zeolites Content (mass% of HAC)	Compressive Strength (MPa) 1 day#	14 days*	28 days*	150 days*	330 days*
1	-	-	-	65	34	36	34	34
2	1.0	A	20.0	62	65	69	72	72
3	3.0	A	47.0	40	64	74	75	-
4	1.6	B	10.0	60	59	57	72	72
5	1.8	C	18.2	49	61	64	69	70
6	1.0	D	15.0	47	47	46	61	62
7	1.8	E	18.2	38	37	42	-	-

*# - moist-cured at 23 °C; * - water-cured at 38 °C after the first 24 hours moist-curing at 23 °C.*

X-ray diffraction analysis: X-ray diffraction analysis was carried out on the HAC pastes containing 4.7% sodium sulfate and 20% zeolite by mass of HAC. Five zeolites comprising mainly clinoptilolites, a chabazite, a stilbite, a natrolite and two molecular sieves were used. The cement paste samples were prepared with a water/solid (HAC + zeolite) ratio = 0.60. The paste samples were cast in 25 mm diameter bottles and rotated for 24 hours at 38 °C. Samples were water-cured at 38 °C after demoulding. X-ray diffraction analysis was carried out on wet samples after grinding in an agate mortar. The test was designed for the comparison of paralliel samples prepared by identical process. The comparison is based on significant differences between parallel samples. Some samples were repeated three times. The relative error of peak height (e.g. C_2ASH_8 at d=1.07 nm, calculated by Rigaku Standard Data Processing software) was 10%. A Rigaku X-ray Diffractometer System Geigerflex D/Max -B was used for x-ray studies.

§ 5.4.2. Results and discussion

The effect of different zeolites on strength development of the HAC/zeolite mortars is shown in Table 5.11.

Table 5.11. Compressive Strength of HAC/Zeolite Mortars

Samples	Compressive Strength (MPa)				
	1 Day#	14 Days*	28 Days*	150 Days*	330 Days*
1	65	34	36	34	34
2	62	65	69	72	72
3	40	64	74	75	-
4	60	59	57	72	72
5	49	61	64	69	70
6	47	47	46	61	62
7	38	34	42	-	-

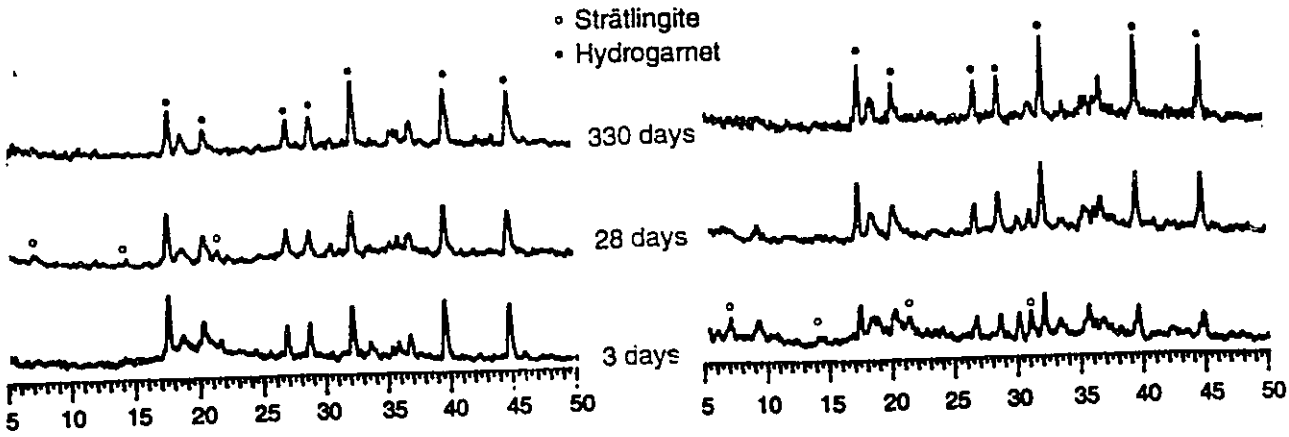
 # - moist-cured at 23 °C;
** - water-cured at 38 °C after the first 24 hours moist-curing at 23 °C.*

The one-day strength was obtained from the specimens moist-cured at 23 °C. Companion specimens were then placed in water at 38 °C. The plain HAC mortar had the highest

compressive strength (65 MPa) at one day. Its strength decreased dramatically to 34 MPa at 14 days due to the conversion reaction. The strength remained at this level until 330 days. The HAC mortar containing 20% zeolite-A and 1.0% sodium sulfate by mass of HAC also had a relatively high one-day strength (62 MPa). The strength continuously increased to 72 MPa at 150 days and maintained this value at 330 days. A high volume addition of zeolite-A (47 mass.% of HAC) resulted in a relatively low one-day strength (40 MPa) of the HAC mortar. Its strength increased significantly at early ages and reached 64 MPa at 14 days and 74 MPa at 28 days. A relatively small content of zeolite-B was used in the HAC mortar sample 4. The one-day compressive strength was 60 MPa and decreased slightly to 57 MPa at 28 days. Further hydration increased the strength to 72 MPa at 150 days. The HAC mortar containing zeolite-C had a one-day strength of 49 MPa. A large strength gain (61 MPa) occurred during the first 14 days of hydration. The strength then increased gradually to 70 MPa at 330 days. Use of Zeolite-D and -E resulted in a relatively low early compressive strength value of less than 50 MPa before 28 days. The ultimate strength of the HAC mortar containing zeolite-D reached 62 MPa at 330 days. The one-day compressive strength of the HAC/zeolite-sodium sulfate mortar can be as high as that of the plain HAC mortar. It is apparent that high early strength, one of the attractive advantages of HAC, can be conserved through use of an HAC/zeolite blended cement. Little or no strength reduction occurred in the HAC mortars containing a zeolite in combination with sodium sulfate.

The x-ray diffraction (XRD) spectra of a plain HAC paste and an HAC paste containing 4.7% sodium sulfate by mass of HAC are shown in Fig. 5.13. Hydrogarnet (C_3AH_6) was formed in both plain HAC and HAC/sodium sulfate pastes at all ages. Hydrogarnet was detected in both the HAC/sodium sulfate paste and plain HAC paste. Small peaks representing strätlingite could be found in the sample containing sodium

sulfate at 3 days (Fig. 5.13b). Sodium sulfate appeared to accelerate the strätlingite formation at 38 °C and early ages. Sodium sulfate alone is not able to inhibit hydrogarnet formation.



Degrees (2θ) Degrees (2θ)

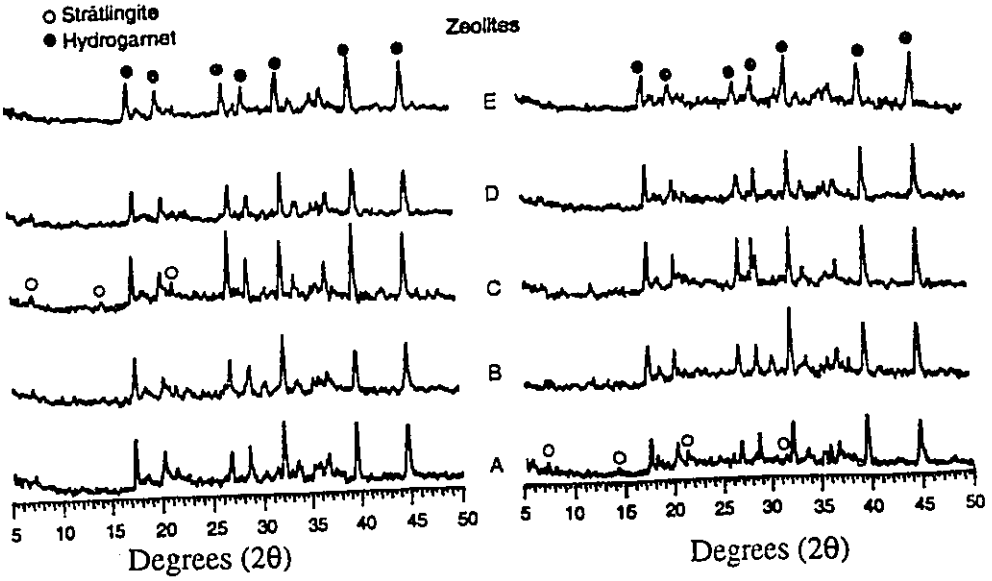
(a) Plain HAC (b) HAC/sodium sulfate

Fig. 5.13. XRD spectra of a plain HAC paste and an HAC paste containing sodium sulfate.

The XRD spectra of HAC/zeolite pastes with or without sodium sulfate are shown in Fig. 5.14. Hydrogarnet were produced in all the HAC pastes containing zeolites (without sodium sulfate) from the different sources (Fig. 5.14a and b). The major component of these zeolites was clinoptilolite. Strätlingite was detected in these samples at 7 days. It was depleted or disappeared at 330 days. It is evident that clinoptilolite-based zeolite alone is not effective in reducing the hydrogarnet formation. Hydrogarnet formation was apparently inhibited in the HAC pastes when sodium sulfate was added in combination with the zeolites (Fig. 5.14c and d). Only a trace of hydrogarnet was found in the pastes containing zeolite-A, B, C or E at 7 days. Little or no hydrogarnet was detected in zeolite-A and C samples at 330 days. Zeolite-D specimens appeared to be less

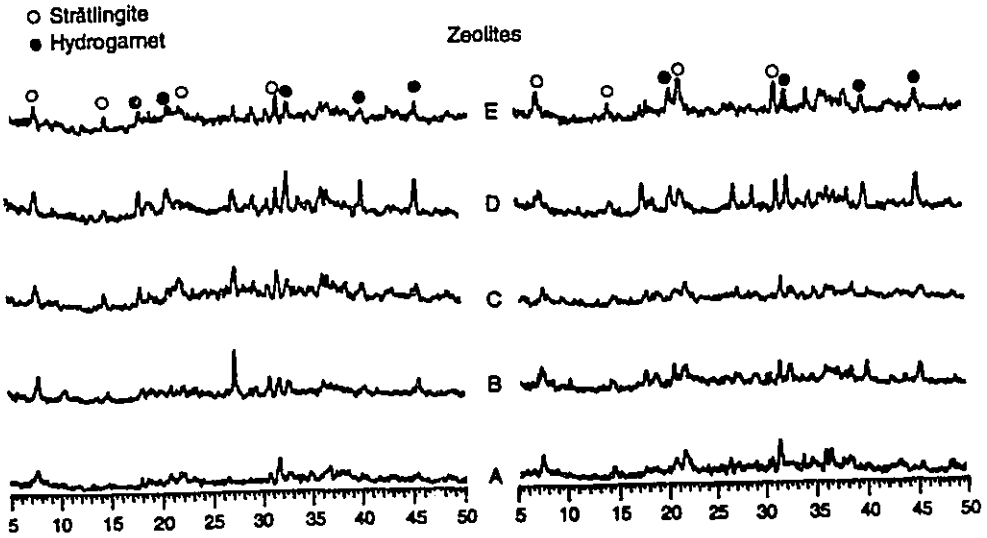
effective in preventing hydrogarnet formation than the other zeolites. Strätlingite was present in the HAC/zeolite pastes containing sodium sulfate.

The effect of zeolite types, e.g. zeolite-A, clinoptilolite; zeolite-F, chabazite; zeolite-G, stilbite; zeolite-H, natrolite, on hydrogarnet and strätlingite formation in the HAC paste with or without sodium sulfate was shown by XRD analysis (Fig. 5.15.). Zeolite addition alone irrespective of type did not limit the hydrogarnet formation (Fig. 5.15a and b). Chabazite appeared to be more favorable for strätlingite formation in the HAC paste. Addition of sodium sulfate in the HAC/zeolite pastes apparently inhibited the hydrogarnet formation (Fig. 5.15c and d). Clinoptilolite and chabazite were evidently more effective in suppressing the hydrogarnet formation than stilbite and natrolite. No hydrogarnet peak was detected in the clinoptilolite and chabazite samples at 7 days. Only very small peaks of hydrogarnet were traced in these samples at 330 days. Hydrogarnet was detected in stilbite and natrolite samples at 7 days. It is apparent that chabazite in combination with sodium sulfate produced more strätlingite than the other zeolites.



(a) HAC/zeolite pastes without sodium sulfate at 7 days

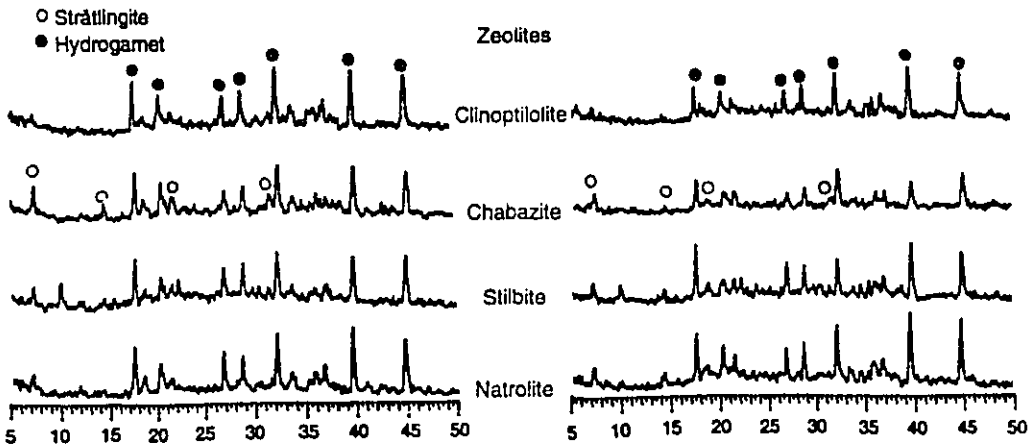
(b) HAC/zeolite pastes without sodium sulfate at 330 days



(c) HAC/zeolite pastes with sodium sulfate at 7 days

(d) HAC/zeolite pastes with sodium sulfate at 330 days

Fig. 5.14 c and d. XRD spectra of HAC pastes containing zeolites from different sources, with or without sodium sulfate.

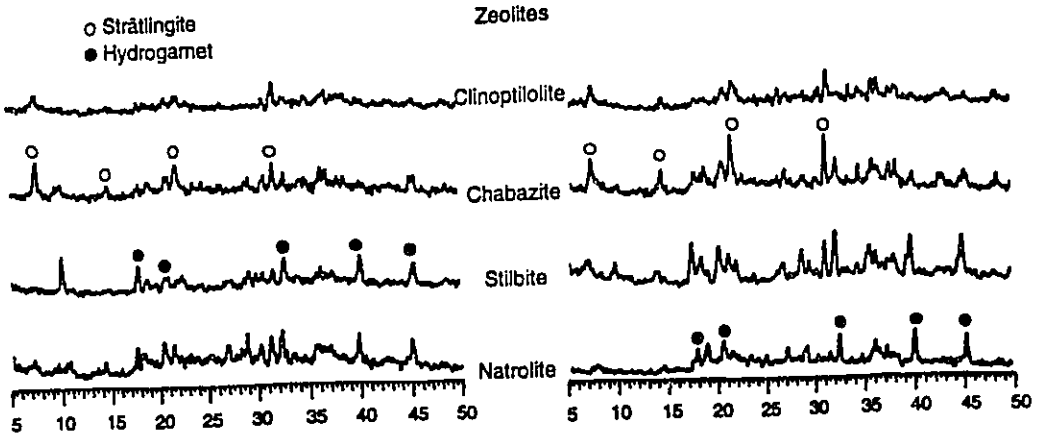


Degrees (2θ)

(a) HAC/zeolite pastes without sodium sulfate at 7 days

Degrees (2θ)

(b) HAC/zeolite pastes without sodium sulfate at 330 days



Degrees (2θ)

(c) HAC/zeolite pastes with sodium sulfate at 7 days

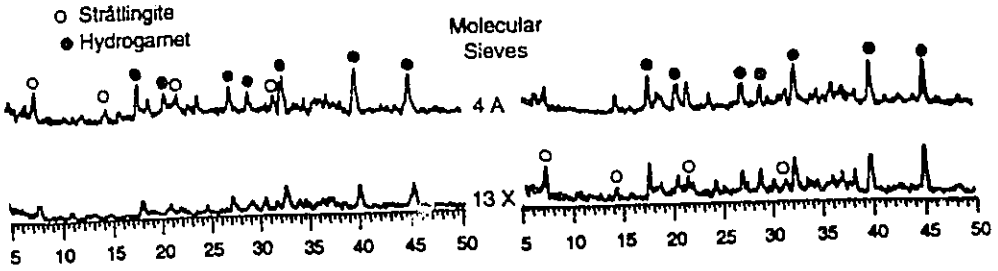
Degrees (2θ)

(d) HAC/zeolite pastes with sodium sulfate at 330 days

Fig. 5.15. XRD spectra of HAC pastes containing different types zeolites, with or without sodium sulfate.

XRD spectra of HAC pastes containing a synthetic zeolite, Type 4A molecular sieve or Type 13X molecular sieve, with or without sodium sulfate are shown in Fig. 5.16. Addition of molecular sieve alone in the HAC paste could not effectively inhibit the formation of hydrogarnet (Fig. 5.16a and b). Strätlingite formed in the HAC/molecular sieve pastes. Much smaller peaks of hydrogarnet were detected in the HAC/molecular sieve pastes containing sodium sulfate than in the samples without sodium sulfate (Fig. 5.16c and d). Molecular sieves promote strätlingite formation in the HAC paste.

Zeolites are a group of minerals containing aluminosilicates. Substitution of different metal ions, e.g. Na^+, K^+, and Ca^{++}, can occur. This may influence the activity of a zeolite in reacting with HAC and forming strätlingite. Highly effective zeolites such as molecular sieves and chabazite will release a sufficient amount of dissolved silicate to produce strätlingite in the hydrating HAC system. These zeolites alone can reduce hydrogarnet formation. However, most of the zeolites are not as effective. Their ability to easily release the dissolved silicate required for strätlingite formation is more limited. Addition of sodium salt in the HAC/zeolite system to activate the reaction of zeolite is necessary in these cases. Prevention of strength reduction of HAC products due to the conventional harmful conversion reactions depends primarily on the silicate release rate of the added siliceous material. Some zeolites are apparently more effective than other siliceous materials such as fly ash, silica fume, etc. A high degree of effectiveness makes it possible to use a relatively low addition of zeolite and still effectively inhibit the strength reduction in HAC products. Low addition of zeolite results in HAC products with high early strength.

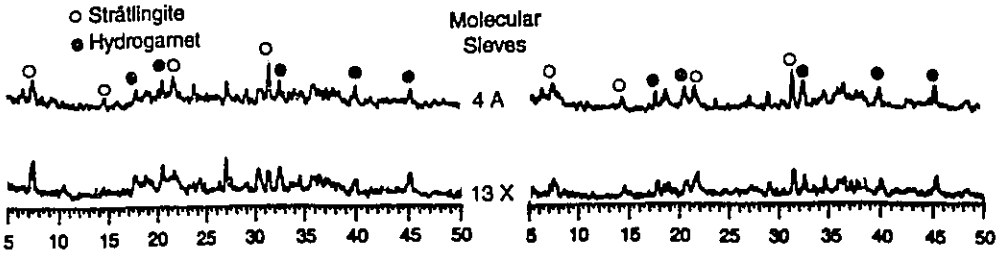


Degrees (2θ)

(a) HAC/zeolite pastes without sodium sulfate at 7 days

Degrees (2θ)

(b) HAC/zeolite pastes without sodium sulfate at 330 days



Degrees (2θ)

(c) HAC/zeolite pastes with sodium sulfate at 7 days

Degrees (2θ)

(d) HAC/zeolite pastes with sodium sulfate at 330 days

Fig. 5.16. XRD spectra of HAC pastes containing different molecular sieves, with or without sodium sulfate.

§ 5.4.3. Conclusions

1. The one-day compressive strength of high alumina cement (HAC) mortars containing certain commercially available zeolites and sodium sulfate, with water/solid ratio 0.4, moist-cured at 23 °C, can be greater than 60 MPa.

2. No strength reduction occurs in HAC mortars containing certain commercially available zeolite and sodium sulfate, with water/solid ratio 0.4, water-cured at 38 °C for 330 days.

3. Hydrogarnet formation is significantly inhibited in HAC paste containing certain commercially available zeolites and sodium sulfate, with water/solid ratio 0.6, water-cured at 38 °C for 330 days.

4. Clinoptiolite or chabazite - based zeolites in combination with sodium sulfate are more effective in preventing the formation of hydrogarnet than stilbite or natrolite - based zeolites in HAC paste.

5. Zeolite addition alone is not able to prevent hydrogarnet formation in HAC paste. The addition of sodium sulfate in combination with zeolite is required.

6. Chabazite is the most effective zeolite in promoting strätlingite formation in HAC paste.

Chapter 6

PROPERTIES OF HIGH ALUMINA CEMENT CONTAINING A CONVERSION-PREVENTING ADDITIVE

- Compressive strength
- Corrosion protection
- Chloride ion penetration

§ 6.1. Introduction

The use of high alumina cement (HAC) has many advantages compared to portland cement. These include high early strength, high temperature resistance and good chemical resistance. It is estimated that the cost of damage to U.S. concrete bridges and parking structures resulting from de-icing salts is about $ 325-1000 million per year [3]. Penetration of chloride ions into reinforced concrete highway structures is mainly responsible for the corrosion. The mobility of chloride ions in OPC and HAC concrete depends on (1) concrete porosity and (2) stability of the calcium aluminate hydrates. It has been reported that the calcium aluminate hydrates derived from tricalcium aluminate (C_3A) in portland cement can bind chloride ions to form a calcium chloro-aluminate hydrate (Friedel's salt) (Monfore and Verbeck, 1960; Baumel, 1960; Mehta, 1977). A high content of C_3A minimizes the degree of reinforcement corrosion by lowering the concentration of corrosion-inducing free chlorides from the pore solution. It does, however, lead to another durability problem in terms of sulfate attack. The synergistic attack resulting from ingress of chloride and sulphate ions causes extreme deterioration of portland cement concrete in a marine environment (Al-Amoudi et al., 1994). Portland cement concrete containing silica fume has a much better resistance to sodium sulfate solutions but is very vulnerable to magnesium sulfate attack (Al-Khaja et al., 1994). The HAC concrete was reported to have high resistance to chloride mobilization (Al-Khaja et al., 1994) and to magnesium sulfate attack (Kurdowski et al., 1990; Majumdar and Singh, 1992). The hexagonal hydrates of HAC will also react with chloride to form Friedel's salt. This significantly reduces the penetration rate of chloride ions into the concrete and delays interaction with the reinforcement. The effect of chloride on the corrosion of reinforcement in HAC mortar was studied by Goni, Andrade and Page (1991). Conversion of calcium aluminate hydrates to hydrogarnet is accelerated in the presence of chloride ions. This makes it ineffective to protect corrosion of the

reinforcement. It is apparent that conversion-inhibited HAC may provide an alternative for corrosion protection of concrete structures in environments containing chloride ions. The purpose of this investigation was to determine the relative effectiveness of this system in reducing corrosion of reinforcing steel in aggressive environments.

§ 6.2. Compressive strength

§ 6.2.1. Experimental

§ 6.2.1.1. Materials

- High alumina cement (HAC): Ciment Fondu, containing SiO_2 4.5%, CaO 39.8%, Fe_2O_3 11.3%, Al_2O_3 41.2%, MgO 0.6%, Na_2O+K_2O 0.1%, produced by Lafarge Calcium Aluminates, Virginia, USA;
- Natural zeolite A: containing mainly clinoptilolite and gismondine, supplied by American Resource Corporation, Inc., California, USA;
- Natural zeolite B: containing mainly clinoptilolite and gismondine, supplied by Polar Powder Technologies, Inc., Alberta, Canada;
- Natural zeolite C: containing mainly clinoptilolite, levyne and offretite, supplied by Zeotech Corporation, New Mexico, USA.

The oxide compositions are listed in Table 6.1.

- Conversion-Preventing Additives (CPA): comprising a natural zeolite and sodium sulfate. Heat-treatment (calcination at about 800 °C for 2 hours) was used during the preparation of selected zeolites. Different CPAs used in this study are listed in Table 6.2.

Table 6.1. Oxide Composition (% by mass) of Selected Natural Zeolites

Oxides	Natural Zeolite		
(% by mass)	A	B	C
SiO_2	69.1	65.8	65.7
Al_2O_3	11.9	14.3	12.5
CaO	0.7	3.4	2.0
Fe_2O_3	0.7	2.6	1.7
MgO	0.4	1.3	0.9
Na_2O	3.5	2.5	1.5
K_2O	3.8	2.7	1.7
MnO	4.9	0.04	0.9

Table 6.2. Different Conversion-Preventing Additives

	Composition (% by mass)		Natural Zeolites	
Additives	Zeolite	Sodium Sulfate	Type	Heat-Treatment
CPA-A	86	14	A	-
CPA-B	86	14	B	-
CPA-B(H)	95	5	B	800 °C for 2h
CPA-C	86	14	C	-
CPA-C(H)	93	7	C	800 °C for 2h

§ 6.2.1.2. Sample Preparation

Compressive Strength Test: Cement mortars were prepared for determination of compressive strength. The sand/cement ratio was 2.75 and the water/solid (HAC + additive) ratio was 0.40. Composition of the specimens is given in Table 6.3. The cement mortar was mixed for 3 minutes and then cast in 50.8x50.8x50.8 mm cube moulds. The

specimens were demoulded after 24 hours moist-curing at 23 °C. The one-day compressive strength was determined after demoulding. Companion specimens were placed in water at 38 °C after demoulding. Compressive strength was determined at designated ages.

Table 6.3. Specimen Composition (arbitrary mass units)

Specimens	HAC	Zeolite *(Type/Content)*	CPA *(Type/Content)*	Sand	Water
Plain HAC	1	-	-	2.75	0.4
Z-A	0.77	**A*/0.23	-	2.75	0.4
Z-B	0.77	*B*/0.23	-	2.75	0.4
CPA-1	0.89	-	***CPA-A*/0.11	2.75	0.4
CPA-2	0.89	-	*CPA-B*/0.11	2.75	0.4
CPA-3	0.89	-	*CPA-C*/0.11	2.75	0.4
CPA-4	0.83	-	*CPA-B(H)*/0.17	2.75	0.4
CPA-5	0.83	-	*CPA-C(H)*/0.17	2.75	0.4
CPA-6	0.67	-	*CPA-C(H)*/0.33	2.75	0.4

**Zeolite A and B contain no addition of sodium sulfate.*

***All CPA materials contain addition of sodium sulfate.*

Microstructure Analysis: Mixes of the HAC pastes for microstructure analysis are listed in Table 6.4. The cement paste samples were prepared with a water/solid ratio = 0.60. The paste samples were cast in 25 mm diameter bottles and rotated for 24 hours at 38 °C. Samples were water-cured at 38 °C after demoulding. X-ray diffraction analysis was carried out on wet samples after grinding in an agate mortar. Fractured surfaces were examined by scanning electron microscopy (SEM). A Rigaku X-ray Diffractometer System Geigerflex D/Max -B was used for X-ray studies. A Cambridge Stereoscan S250 Scanning Electron Microscopy was employed for SEM investigations.

Table 6.4. HAC Pastes Used for Microstructure Analysis

Samples	HAC	Zeolite *(Type/Content)*	Additive *(Type/Content)*	Water
1	1	-	-	0.6
2	0.83	*A*/0.17	-	0.6
3	0.83	*B*/0.17	-	0.6
4	0.83	*C*/0.17	-	0.6
5	0.80	-	*CPA-A*/0.20	0.6
6	0.80	-	*CPA-B*/0.20	0.6
7	0.80	-	*CPA-C*/0.20	0.6

§ 6.2.2. Results and discussion

The effect of zeolites on the strength of high alumina cement (HAC) mortars is shown in Fig. 6.1. The compressive strength of plain HAC mortar was about 65 MPa after 24 hours moist-curing at 23 °C. Strength then decreased to about 35 MPa after 14 days water-curing at 38 °C. A slight strength recovery occurred after 14 days. The compressive strength of HAC mortar containing 30 % zeolites by mass of HAC was about 55 MPa after 24 hours moist-curing at 23 °C. The strength reduction at 14 days of HAC mortar containing Zeolite-A compared to plain HAC mortar appeared to be slightly reduced. Little or no difference of strength reduction between ZeoliteA and Zeolite B HAC mortar at 14 days was found. Zeolite appears to accelerate the strength recovery at later ages. The 150-day strengths of HAC mortar containing Zeolite A or Zeolite B were all slightly higher than the plain HAC mortar. Evidence for invocation of the conversion reaction was also provided by the x-ray diffraction (XRD) analysis of each HAC paste after 60 days of water-curing at 38 °C (Fig. 6.2). Cubic hydrogarnet

(C_3AH_6) crystals were found to be the major mineral phase present in all the samples. The hydrogarnet formation corresponds to the strength reduction.

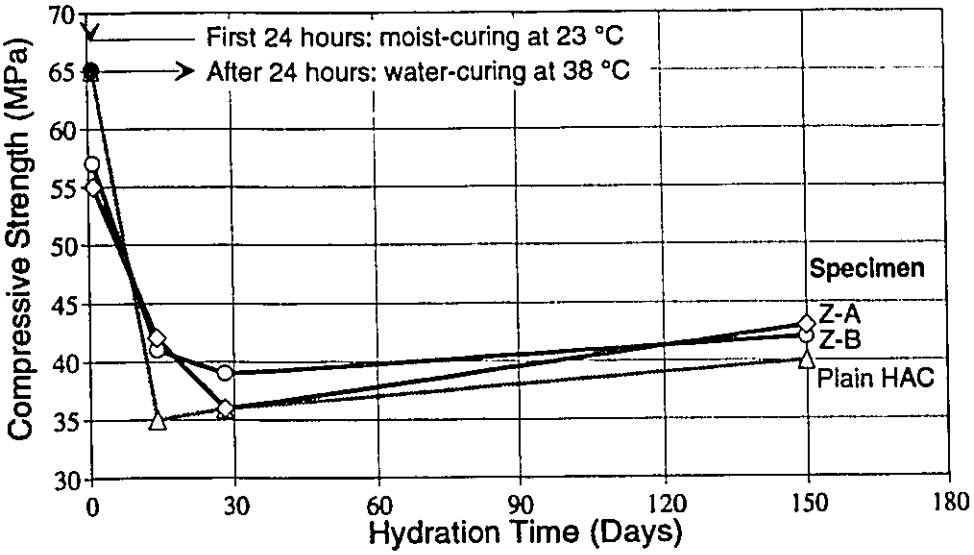


Fig. 6.1. Effect of zeolite addition on compressive strength development of HAC mortars.

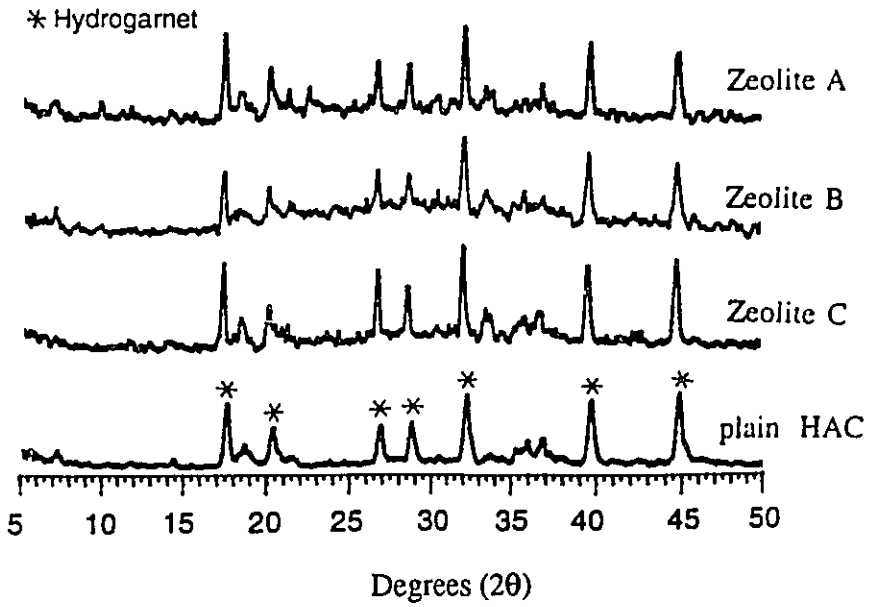


Fig. 6.2. The XRD spectra of the HAC pastes containing zeolites at 60 days.

The effect of a conversion-preventing additive (CPA) on strength development of HAC mortars is shown in Fig. 6.3 (refer also to table 6.4). It was found that the strength reduction of HAC mortar was prevented by using about 12% CPA by mass of HAC. The one-day strength of HAC mortar containing CPA-A additive was 60 MPa. Very little strength development occurred from one day to 28 days. Strength increased to 72 MPa at 150 days. The one-day strength of HAC mortars containing CPA-B additive was about 43 MPa. Its strength increased to 51 MPa in 28 days. No further strength change was found after 28 days. A large strength increase was recorded for the HAC mortar containing CPA-C additive. Its 28- and 150-day strength values were 57 and 65 MPa respectively.

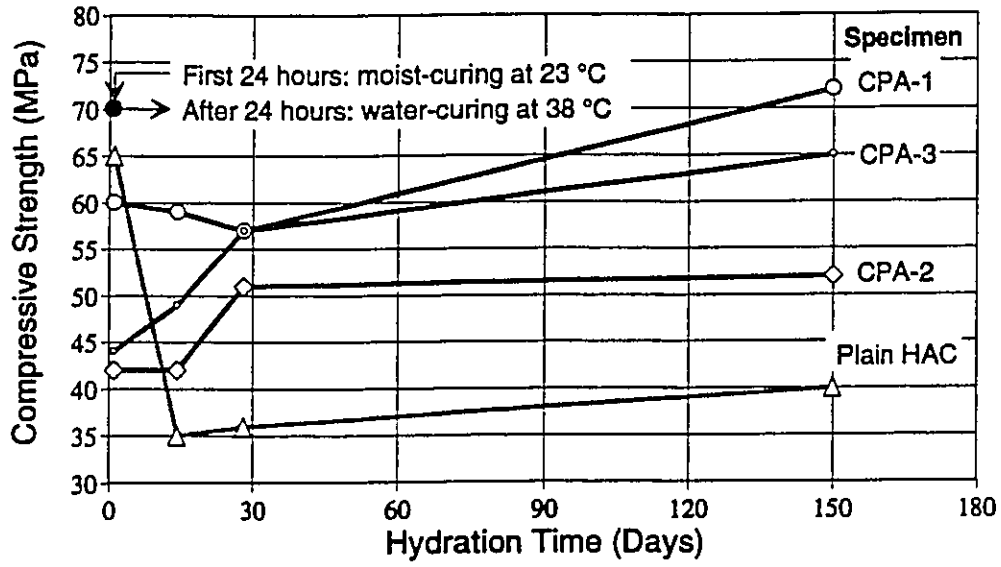


Fig. 6.3. The effect of conversion-preventing additives on compressive strength development of HAC mortars. Specimen composition is given in Table 6.2.

Heat-treatment of the conversion-preventing additives (refer to table 6.3) appeared to result in significant improvement in strength development of the HAC mortars (Fig. 6.4). High strength developed in all the samples during 28 days of hydration. A significant strength increase was found in the HAC mortar specimens

containing 50% by mass of HAC CPA-C(H) additive. Its strength increased from 45 MPa at 1 day to 71 MPa at 14 days. The strength gain rate decreased after 14 days. The 28-day and 150-day strengths were 74 and 75 MPa respectively. Decrease of CPA-C(H) additive addition (e.g. 20% by mass of HAC) greatly increased one-day strength to about 62 MPa. It, however, resulted in less strength gain at later ages. Its strength values at 14, 28 and 150 days were 65, 69 and 72 MPa respectively. The one-day strength of the HAC mortar containing 20% CPA-B(H) additive was much less than that containing 20% CPA-C(H) additive. Its strength increased from 49 MPa at 1 day to 61 MPa at 14 days. The strength then slowly developed to 64 MPa at 28 days and to 68 MPa at 150 days.

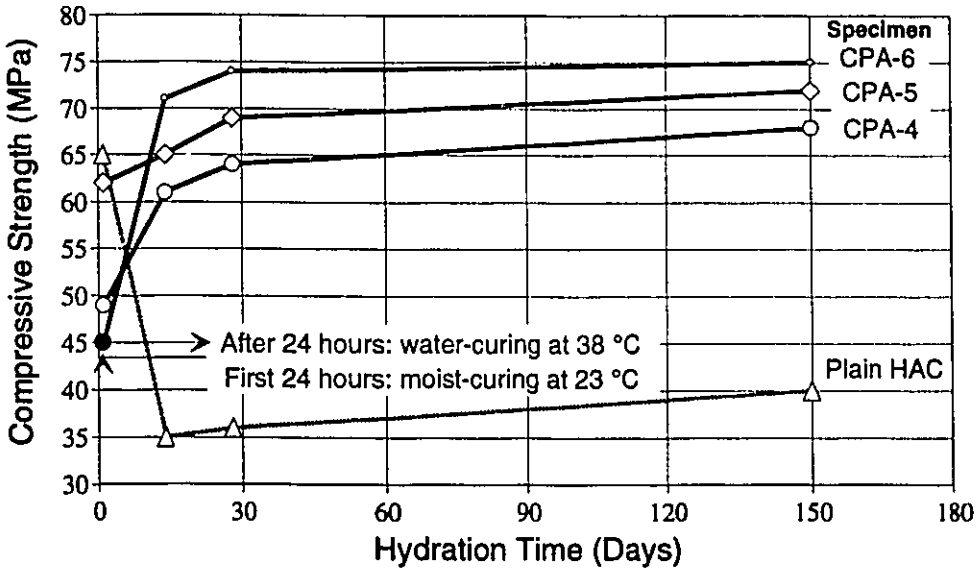


Fig. 6.4. The effect of heat-treated conversion-prevention additives on compressive strength development of the HAC mortars. Composition is given in Table 6.2.

The HAC concrete structure may not initially be cured at elevated temperature in practice. Strength reduction of the HAC concrete due to conversion occurs at later ages when the ambient temperature increases, e.g. in summer. The effect of a temperature

shift from low to high on the strength change of the HAC mortars with age was studied (Fig. 6.5 and 6.6). The specimens were moist-cured at 23 °C for the first 28 days followed by water-curing at 38 °C. The dashed and solid curves represent 23 °C moist-curing and 38 °C water-curing respectively in Fig. 6.5 and 6.6. It is believed that most of the HAC clinker has hydrated to form C_2AH_8 (28 days at 23 °C) since the hydration rate of HAC is fast. Significant strength reduction was found in the plain HAC mortar after the curing temperature shifted to 38 °C. The compressive strength decreased from 72 MPa at 28 days (moist-curing at 23 °C) to about 40 MPa at 60 days (following water-curing at 38 °C after the first 28 days). Further strength reduction from 60 days to 150 days was minimal.

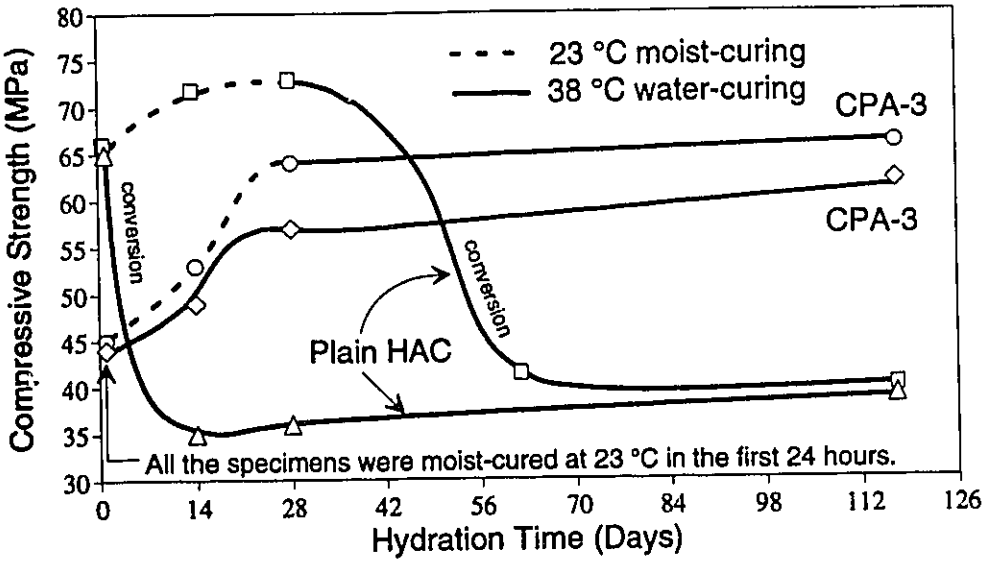


Fig. 6.5. The effect of curing condition on compressive strength development of the HAC mortar containing a conversion-preventing additive (see table 6.3).

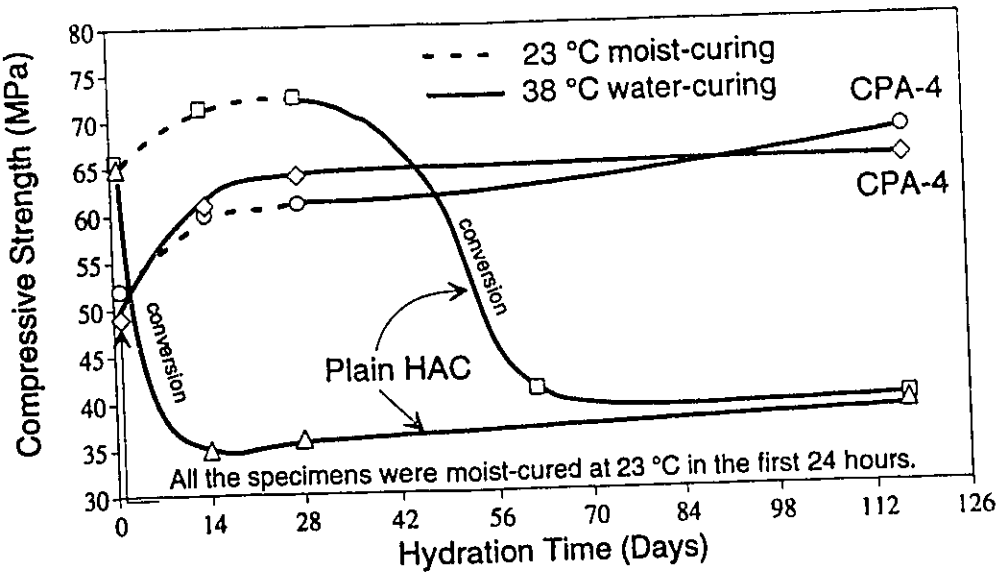


Fig. 6.6. The effect of curing condition on compressive strength development of the HAC mortar containing a heat-treated conversion-preventing additive (see table 6.3).

No strength reduction was found in the HAC mortar containing a CPA additive after the curing condition shifted from 23 °C moist-curing to 38 °C water-curing. The HAC mortar containing the CPA-C additive and moist cured at 23 °C had higher strength than the water-cured mortar at 38 °C from 1 day to 28 days (Fig. 6.5). There was a slight difference in the compressive strength of the HAC mortars containing the heat-treated CPA-B(H) additive at the two different initial curing conditions (Fig. 6.6). The strength of all the specimens increased slowly from 28 days to 150 days when cured at 38 °C.

The XRD spectra of the HAC pastes containing different conversion-preventing additives (comprising different types of zeolite) are shown in Fig. 6.7. Little or no hydrogarnet was detected in the HAC pastes containing CPA. Strong peaks corresponding to the strätlingite phase were found in these samples. Strätlingite formation during HAC hydration has been reported to have a role in the prevention of

strength reduction in HAC products. The role of the sodium salt component of the

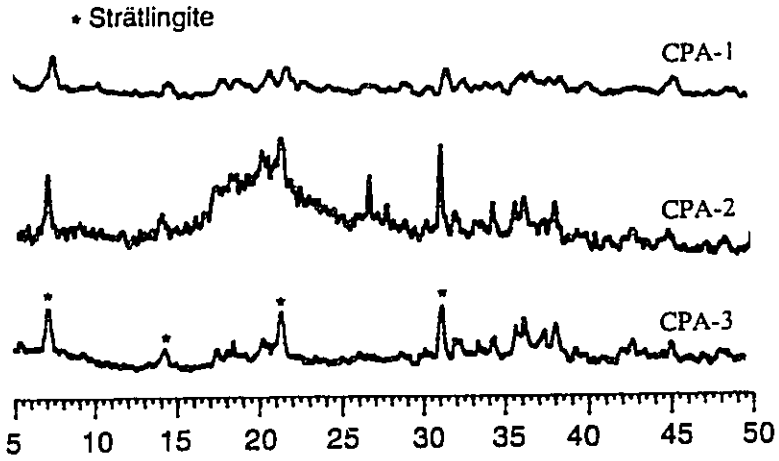


Fig. 6.7. The XRD spectra of the HAC pastes containing different conversion-preventing additives at 28 days (see table 6.3).

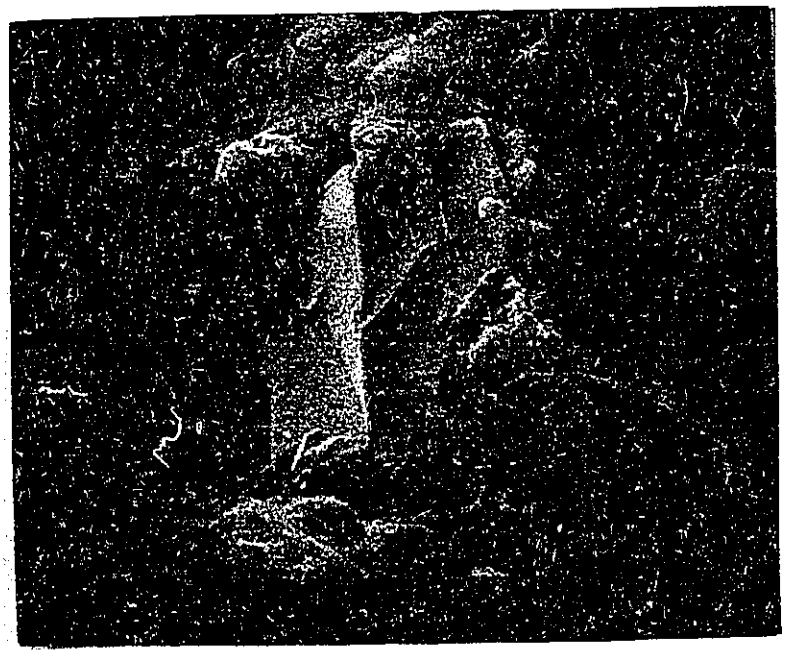


Fig. 6.8. SEM micrographs of the HAC paste containing a CPA-C additive at 60 days.

conversion-preventing additives has been studied. It appears that crystallization of hexagonal strätlingite plates in hydrated high alumina cement systems containing zeolites was significantly accelerated in the presence of sodium ions. Its amount is greatly increased. Sodium ions appeared to play a significant role in strätlingite formation in HAC - zeolite systems. It was postulated that crystallization of strätlingite results from the reaction between CAH_{10} or C_2AH_8 and dissolved silica. Sodium ions promote increased dissolution of silica required for strätlingite formation. Hydration of zeolites in HAC paste without addition of sodium salt was relatively slow. Strätlingite nucleation and crystallization appears to be dependent on the dissolved silica concentration in the HAC - zeolite system. Strength reduction was prevented when strätlingite formed in preference to hydrogarnet. Well developed plate-like strätlingite crystals were commonly found in the HAC paste containing CPA additives. A typical SEM micrograph showing the presence of strätlingite in an HAC paste containing 20% CPA-C additive by mass of the HAC is presented in Fig. 6.8.

§ 6.2.3. Conclusions

1. The use of newly developed conversion-preventing additives (CPA) in HAC mortars can effectively prevent strength reduction due to conversion of hexagonal aluminate hydrates to hydrogarnet. The effective addition of CPA in HAC mortar ranges from 12 to 50 % by mass of HAC.

2. Strätlingite rather than hydrogarnet is preferentially formed in HAC paste containing CPA.

3. The one-day compressive strength of HAC mortar containing CPA and moist-cured at 23 °C ranges from 40 to 60 MPa.

4. The compressive strength of HAC mortar water-cured at 38 °C and containing CPA slowly increases with the hydration time.

5. Addition of heat-treated CPA to HAC mortar results in much higher one-day compressive strength values than non-heat-treated CPA.

6. Increase of heat-treated CPA content in amounts greater than 50% in the HAC products decreases the one-day compressive strength values but significantly increases strength after 14 days.

7. A shift in curing temperature from initially low to finally high values does not adversely affect strength development of HAC mortar containing CPA.

§ 6.3. Corrosion Protection of Reinforced Mortars in Calcium Chloride Solution

§ 6.3.1. Experimental

§ 6.3.1.1. Steel bar Corrosion

Steel bar (8 mm in diameter and 149 mm long) was used as reinforcement and positioned in the center of prism specimens 25x25x152 mm. The steel bar contained approximately 99.82% Fe and 0.18% C. The minimum thickness of the mortar cover, e.g. OPC, HAC or HAC/CPA, on the steel bar was 8.5 mm. The specimens were moist-cured at 38 °C (100 °F) for 28 days and then subjected to drying/wetting (d/w) cycles. The d/w regime was 4 days drying and 6 days exposure to calcium chloride solutions (Cl^- concentration = 3 mol/L). The steel bars were extracted by breaking the mortars after 14 d/w cycles. Corroded patterns of the steel bars were carefully drawn on squared paper and the percentage of rusted area was estimated. A pull-out test was also carried out on each specimen.

§ 6.3.1.2. Pore structure

Mortar samples were taken up at a 5 mm (0.2 in) depth from the outer-surface of the mortar bars for the measurement of mercury intrusion pore size distribution analysis after 14 d/w cycles. Mortar particles 3-5 mm (0.12-0.20 in) in diameter were used for the mercury intrusion test. The mercury intrusion analysis was carried out using an Quanta Chrome Autoscan-33 Porosimeter.

§ 6.3.1.3. Chloride ion penetration

Mortar samples were taken using the same procedure as described above. Ground mortar powder was used for Cl^- concentration determination. The free-Cl^- concentration was determined by an extraction method after Mindess and Young (1981). The samples for measuring combined chloride ion were prepared according to ASTM C 114-88. The chloride ion concentrations were determined by an Orion pH/ISE meter, Model 720A.

§ 6.3.2. Results and discussion

Photographs of the steel bars are shown in Fig. 6.9. The properties of the cement mortars including the steel bar-mortar bond strength, Cl^- concentration, rusted area of the steel bar and total porosity, are given in Table 6.5. The pore size distribution of different mortars is shown in Fig. 6.10.

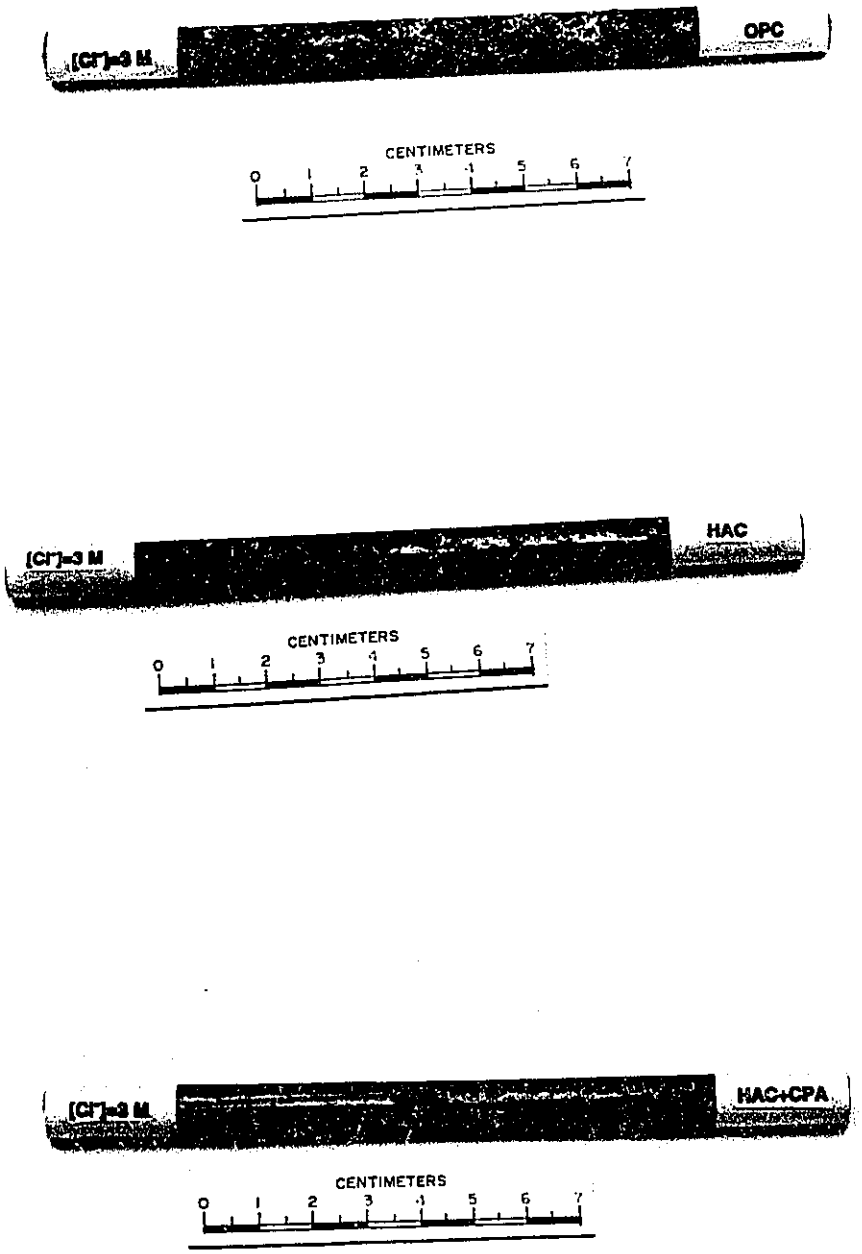


Fig. 6.9. Photographs of the steel bars.

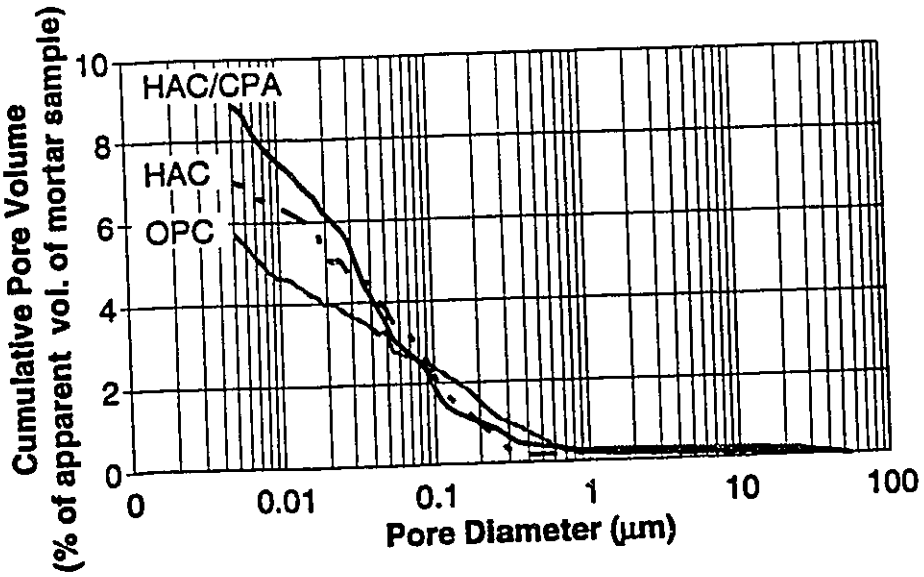


Fig. 6.10. The pore size distribution of different mortars used in the corrosion studies.

Table 6.5. Durability Related Properties of the Cement Mortars

Properties	OPC	HAC	HAC/CPA
Steel Bar-Mortar Bond Strength (MPa)	7.9	5.1	10.1
Cl^- Concentration (kg/m^3)			
Free	29.4	27.3	14.7
Combined	4.7	1.8	1.9
Rusted Area of Steel Bar (%)	83	88	5
Total Porosity (%)	5.72	7.09	8.99

The HAC/CPA mortar had a higher bond strength to the steel bar than the OPC mortar. The HAC mortar after conversion had a low bond strength. The total porosity of the HAC/CPA mortar was higher than the OPC or HAC mortars. This was due largely to the increase of pores with a diameter less than 0.1 μm. The volume of pores with

diameter larger than 0.1 μm in the HAC/CPA mortar was slightly less than that in the OPC mortar. The free-Cl^- concentration in the HAC mortar was slightly lower than that in the OPC mortar and about double that of the HAC mortar containing CPA. A large value of free-Cl^- concentration might be the result of the d/w cycles in concentrated calcium chloride solution. The amount of combined-Cl^- in the OPC mortar was much higher than that in the other mortars. The Cl^- penetration rate in HAC and OPC mortars appeared to be similar, since they had similar values of free-Cl^- concentration. It was concluded that the HAC hydrates after conversion have a reduced ability to combine with Cl^- relative to the OPC hydrates. The HAC/CPA system was apparently effective in reducing the Cl^- penetration. This resulted in a much lower free-Cl^- concentration at the same depth in the mortar. The HAC/CPA mortar had a low Cl^- penetration rate. Nevertheless there was a relatively high amount of combined Cl^-, compared to the HAC mortar was present. It was evident that the HAC/CPA mortar had a high potential to bind Cl^-. Correspondingly, the HAC/CPA mortar had excellent corrosion protection characteristics (see Fig. 6.9). The rusted area of the steel bar in the HAC/CPA mortar was only 5%. Areas in the OPC or HAC mortar were all higher than 80%.

§ 6.3.3. Conclusion

High alumina cement mortar after conversion appears to be unable to protect the reinforcement from corrosion in an environment containing chloride ions. Conversion inhibited high alumina cement appears to have excellent behavior in corrosion protection of reinforcement under severe test conditions. The HAC/CPA mortar can effectively resist the penetration of chloride ions.

Chapter 7

SUMMARY AND CONCLUSIONS

- Mechanisms of Strätlingite formation
- Conversion-Preventing Additives (CPA)
- Engineering Properties

§ 7.1. Summary

The original work reported in this thesis is mostly experimental. Extensive laboratory tests were carried out to investigate the mechanisms of strätlingite formation in the high alumina cement - silicious materials - water system and to develop conversion preventing additives for high alumina cement products. Fundamental research on the mechanisms of strätlingite formation are reported in Chapters 3 and 4. Formulations and properties of conversion inhibited high alumina cements are reported in Chapters 5 and 6.

§ 7.2. Mechanisms of Strätlingite formation

Sodium ions play a significant role in strätlingite formation in HAC - siliceous material -water systems. Crystallization of strätlingite results from the reaction between CAH_{10} or C_2AH_8 and dissolved silica. Hydration of siliceous materials in HAC paste without addition of sodium salt is relatively slow. Sodium ions promote increased dissolution of silica required for strätlingite formation.

Addition of siliceous materials, such as natural zeolites, silica fume, fly ash or ground granulated blast-furnace slag, in combination with a sodium salt, e.g. sodium sulfate, in HAC paste can induce the formation of strätlingite. This competitive reaction prevents traditional conversion from hexagonal calcium aluminates to cubic hydrogarnet when the HAC paste is water cured at 38 °C. Addition of sodium sulfate increases the pH value of the HAC - siliceous materials hydration system to values above 12. A pH value higher than 12 is a potential indicator of strätlingite formation in the HAC - siliceous materials system.

§ 7.3. Conversion-Preventing Additives (CPA)

The CPA comprises 80-99 wt.% siliceous material and 20-1 wt.% inorganic salt, to be used in high alumina cement products. Strätlingite (C_2ASH_8) is produced from hydration reactions between high alumina cement and the conversion-preventing

additive. The hydration of the siliceous material in high alumina cement system can be activated by the inorganic salt. The siliceous pozzolan is one of the following materials: zeolite group minerals, calcined zeolites, granulated blast-furnace slag, fly ash, silica fume, metakaolin and rice hull ash. The inorganic salt contains sodium or potassium cations and one or more of following anions: sulphate, carbonate, nitrate, silicate, phosphate, bromide and chloride. The zeolite group minerals are any natural or synthetic minerals having the general formula:

$$(M^{+}_{2}, M^{2+})\ O \cdot xAl_2O_3 \cdot ySiO_2 \cdot zH_2O.$$

M^{+} is usually Na or K; M^{2+} is Mg, Ca, or Fe. The calcined zeolites are the zeolite group minerals after calcination at 600-1000 °C for 1-3 hours.

§ 7.4. Engineering Properties of High Alumina Cement Products Containing a CPA

The use of conversion-preventing additives (CPA) in HAC mortars can effectively prevent strength reduction due to conversion of hexagonal aluminate hydrates to hydrogarnet. The effective addition of CPA in HAC mortar ranges from 12 to 50 % by mass of HAC. A conversion inhibited high alumina cement product containing a CPA has a one-day compressive strength value in the range 40-60 MPa when moist-cured at 23 °C. It has little or no compressive strength reduction or gradually increasing strength when water-cured at 38 °C.

Conversion inhibited high alumina cement has excellent behavior in corrosion protection of reinforcement under severe test conditions. The HAC/CPA mortar can effectively resist the penetration of chloride ions.

REFERENCES

Al-Amoudi, O. S. B., Rasheeduzzafar, Maslehuddin, M., and Abduljauwad, S. N., "Influence of chloride ions on sulphate deterioration in plain and blended cements", Magazine of Concrete Research, Vol.46, No.167, pp.113-123, (1994).

Al-Khaja, W. A., Rasheeduzzafar, W. A., Al-Sayed, M. H., and Al-Khoder, A. A., "Sulfate resistance and chloride penetration characteristics of high-strength concrete", High-Performance Concrete, Proc. ACI Intl. Conf., Singapore, SP-149, pp.123-134, (1994).

Baumel, A., "Effect of calcium chloride on the corrosion behavior of steel in concrete", Beton Herstellung-Verwendung (Dusseldorf), V.10, p.256, (1960).

Bensten, S., "pH in calcium aluminate cement with varying microsilica content", Institutt for silicaog hϕytemperaturkjemi, Norges Tekniske Hϕyskole (1984).

Bentsen, S., Seltveit, A., "Effect of microsilica on conversion of high alumina cement", *Calcium Aluminate Cements*, Chapman and Hall, London, UK, pp.294-319, (1990).

Bhaskara, Rao, P., and Viswanathan, V. N., "Chemistry of arresting strength retrogression in structural high - alumina cement", Int. Congr. Chem. Cem.,[Proc.], 7th, Vol.3, V/51-V/56. SEPTIMA: Paris, Fr.(1980).

Bradbury, C., Callaway, P. M., and Double, D. D, "The conversion of high alumina cement/concrete", Mater. Sci. Eng., 23 (1), pp.43-53 (1976).

Edmonds, R. N.; Majumdar, A. J., "The hydration of mixtures of monocalcium aluminate and blast-furnace slag", Cem. Concr. Res., 19 (5), pp.779-782 (1989).

Fentiman, C. H., Rashid, S., "The effect of curing conditions on the hydration and strength development in Fondu : Slag", *Calcium Aluminate Cements*, Chapman and Hall, London, UK, pp.272-281, (1990).

George, C. M., "Manufacture and preformance of aluminous cement: a new prespective", *Calcium Aluminate Cements*, Chapman and Hall, London, UK, pp.181-207, (1990).

Goni, S., Andrade, C., and Page, C. L., "Corrosion behaviour of steel in high alumina cement mortar samples: effect of chloride", Cem. Conr. Res., Vol. 21, 1991, pp.635-646.

Kurdowski, W., Taczuk, L., and Trybalska, B., "Behaviour of high alumina cement in chloride solutions", *Calcium Aluminate Cements*, Chapman and Hall, New York, pp.222-229, (1990).

Lea, F. M., *The Chemistry of Cement and Concrete*, Third edition, Edward Arnold (Publishers) Ltd., p.519,(1970).

Lea, F. M., *The Chemistry of Cement and Concrete*, Third edition, Edward Arnold (Publishers) Ltd., pp.503-504,(1970).

Lea, F. M., Desch, C. H., *The Chemistry of Cement and Concrete*, Second editor Edward Arnold (Publishers) Ltd., pp.431-437.

Marcdargent, S., Testud, M., Bayoux, J. P. and Mathieu, A., "Hydration and strength of blends CAC-fume silica and stability of hydrates", 9th ICCC, Vol. IV, pp.651, (1992).

Majumdar, A. J. Edmonds, R. N., and Singh, B., "Hydration of calcuim alumiates in presence of granulated blastfurnace slag", *Calcium Aluminate Cements*, Chapman and Hall, London, UK, pp.259-271, (1990).

Majumdar, A. J., Singh, B., "Gehlenite octahydrate-forming cement blends", Eur. Pat. Appl., 9 pp.(1989).

Majumdar, A. J., Singh, B., Tech, M. and Edmonds, R. N. "Blended high-alumina cements", Ceram. Trans., Vol. 16 (Adv. Cem. Mater.), pp. 661-678, (1991).

Majumdar, A. J., Singh, B., "Properties of some blended high-alumina cements", Cem. Concr. Res., Vol. 22, pp. 1101-1114, (1992).

Marjumdar, A. J., edmonds, R. N., Singh,B."Hydration of Secar 71 aluminous cement in presence of granulated blast furnace slag", Cem. Concr. Res., Vol.20 (1), pp. 7-14 (1990).

Mehta, P. K., "Effect of cement composition on corrosion of reinforcing steel in concrete", Chloride Corrosion of Steel in Concrete, STP-629, ASTM, Philadelphia, pp.12-19, (1977).

Midgley, H. G., "High alumina cement in construction - a future based on experience", *Calcium Aluminate Cements*, Chapman and Hall, London, UK, pp.1-13, (1990).

Midgley, H. G., "Measurement of high - alumina cement-calcium carbonate reactions using DTA", Clay Miner., 19 (5), pp.857-864 (1984).

Midgley, H. G., "The relationship between cement clinker composition and strength recovery of hydrating high-alumina cement during conversion", Int. Congr. Chem., [Proc.], 7th, Vol. 3, V/68-V/70. SEPTIMA: Paris, Fr. (1980).

Midgley, H. G., Rao, P. B., "Formation of strätlingite, $2CaO.SiO_2.Al_2O_3.8H_2O$, in relation to the hydration of high alumina cement", Cement and Concrete Research, Vol. 8, pp.169-172, 1978.

Monfore, G. M., and Verbeck, C. J., "Corrosion of prestressed wire in concrete", ACI J., Proc. Vol.57, No.5, Nov., pp.491-516 (1960).

Quon, D. H. and Malhotra, V. M., "Effect of elevated temperatures on compressive strength, pulse velocity and conversion of high alumina cement concrete", Canmet Report, Canada Cent. Miner. Energy Technol., Dep. Energy, Mines Resour., Ottawa, Ont. Can., 77 - 49, 58 pp.(1977).

Quon, D. H. and Malhotra, V. M., "Effect of superplasticizers on slump, strength, and degree of conversion of high alumina cement concrete", Publ. SP - Am. Concr. Inst., 68 (Dev. Use Superplast.), pp.173-187 (1981).

Rao, P. B., Viswanathan, V. N., "Chemistry of arresting strength retrogression in structural high-alumina cements", Int. Congr. Chem. Cem., Proc., 7th, Vol. 3, V/51-V/56. SEPTIMA: Paris, France, (1980).

Revay, M., Wagner, Z., "Study of expected strength changes of concrete structures made of Hungarian high-alumina cement and resulting conclusions", Epitoanyag, 37 (11), pp. 321-330 (1985).

Richardson, I. G. and Groves, G. W., "The microstructure of blastfurnace slag/high alumina cement pastes", *Calcium Aluminate Cements*, Chapman and Hall, London, UK, pp.282-293, (1990).

Singh, B., Majumdar, A. J., "The hydration of calcium dialuminate and its mixtures containing slag" Cem, Concr. Res., Vol. 22 (6), pp.1019-1026, (1992).

Taylor, H. F. W., *The Chemisty of Cenments*, Academic press, London, UK, Vol.2, p.14, (1964).

Taylor, H. F. W., *Cement Chemistry*, Academic press, London, UK, p.317, (1990).

Taylor, H. F. W., "Microstructural development in pastes of a calcium aluminate cement", *Calcium Aluminate Cements*, Chapman and Hall, London, UK, pp.41-51, (1990).

Taylor, H. F. W., *Cement Chemistry*, Academic press, London, UK, pp.317-319, (1990).

Wojciech, G. P., "The effect of limestone fillers on sulphate resistance of high alumina cement composites", *Calcium Aluminate Cements*, Chapman and Hall, London, UK, pp.241-254, (1990).