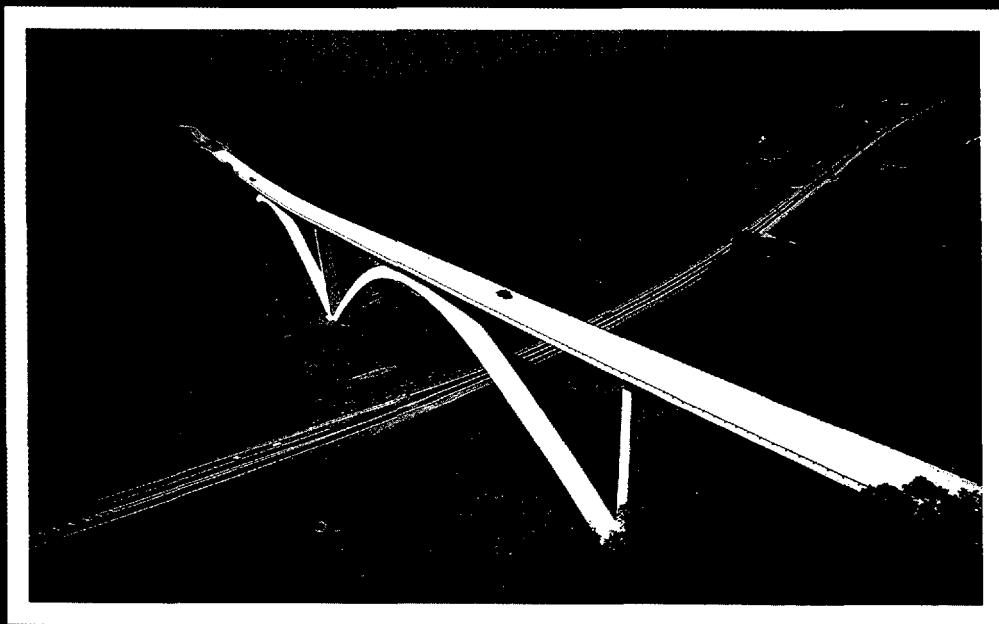


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**FIFTH CANMET/ACI
CINQUIÈME CANMET/ACI**

INTERNATIONAL › CONFÉRENCE › INTERNATIONALE



**SUPERPLASTICIZERS
AND OTHER
CHEMICAL ADMIXTURES
IN
CONCRETE**

**LES SUPERPLASTIFIANTS
ET AUTRES
ADJUVANTS CHIMIQUES
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Superplasticizers and Other Chemical Admixtures in Concrete

**Proceedings
Fifth CANMET/ACI
International Conference
Rome, Italy, 1997**

Editor
V. M. Malhotra



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PREFACE

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

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

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

In October 1994, CANMET in association with the American Concrete Institute sponsored the fourth conference on the subject in Montreal, Canada. The objective of this conference was to bring to the attention of the concrete community the new developments in chemical admixtures since the last conference in 1989. The proceedings of the conference were published as ACI special publication SP-148.

In October 1997, the Council for the Organization of CAMNET/ACI Conferences in association with American Concrete Institute and several cement and concrete organizations in Italy sponsored the fifth conference on the subject in Rome, Italy. This conference was aimed at transferring technology in the fast-moving field of chemical admixtures. A total of more than 60 papers from more than 20 countries were received and reviewed by the ACI review panel and 49 were accepted for publication in the proceedings of the conference. The proceedings were published as ACI special publication SP-173. The cooperation of the authors in accepting the reviewers' suggestions is greatly appreciated.

A special symposium was held in conjunction with this conference to honour Prof. Mario Collepardi, University of Ancona, Italy. The proceedings of this symposium were published as a separate volume for distribution at the conference.

During the conference a special dinner was held to recognize Prof. Raymundo Rivera-Villarreal, Universidad Autonoma de Nuevo Leon, Monterrey, Mexico for his long-term contributions in the area of concrete technology in general and chemical admixtures in particular.

Thanks are extended to the members of the review panel for their contributions towards the publication of this volume.

The help and assistance of A. Bilodeau (Chairperson), B. Fournier, R. Chevrier (Members) of the Slide Review Panel are gratefully acknowledged. Thanks are also extended to Harry S. Wilson, Maria Venturino, and Gordon D. Brearley for their help in the processing of the manuscripts, both for the ACI proceedings and the supplementary volume. Acknowledgement is also made to Helayne Beavers, Managing Editor, Journals and Special Publications, for her help in getting the proceedings ready on time.

V.M. Malhotra, P.Eng.

Editor

Chairman, Fifth CANMET/ACI International Conference
on Superplasticizers and Other Chemical Admixtures in Concrete

October 1997

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Mechanical Properties of Modified Reactive Powder Concrete

by S. Collepardi, L. Coppola, R. Troli and M. Collepardi

Synopsis: Original Reactive Powder Concrete (*RPC*) - in form of a superplasticized cement mixture with silica fume, steel fibers and ground fine quartz (150-400 μm) - was studied in comparison with a modified *RPC* where a graded natural aggregate (max size 8 mm) was used to replace the fine sand and/or part of the cementitious binder.

Original and modified *RPC* were manufactured at a plastic-fluid consistency, cast by vibration and cured at three different conditions: *a*) room temperature; *b*) steam-curing at 90°C; *c*) high pressure steam-curing at 160°C.

The addition of the graded aggregate does not reduce the compressive strength provided that the quality of the cement matrix, in terms of its water-cement ratio, is not changed. This result is in contrast with the model proposed to relate the high compressive strength level of *RPC* (200 MPa) to the absence of coarse aggregate.

Both the original and modified *RPC* (with the coarse aggregate addition) perform better - in terms of higher strength and lower drying shrinkage or creep strain - when they are steam cured rather than cured at room temperature. This improvement was related to a more dense microstructure of the cement matrix, particularly in the *RPC* specimens steam cured at 160°C.

Keywords: Creep properties; flexural strength; high-strength concrete; shrinkage; silica fume; steels; superplasticizers; toughness

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Silvia Collepari is a research civil engineer of Enco, Spresiano, Italy. She is working in the field of superplasticized concrete mixtures and has published a couple of papers in this area.

Luigi Coppola is a research civil engineer and technical director of Enco. He has authored numerous papers on various aspects of concrete technology, durability and mix-design.

Roberto Troli is a research civil engineer and director of the Enco laboratory. He is author of several papers in the field of concrete technology and in particular of chemical and mineral admixtures.

Mario Collepari is Professor of Materials Technology and Applied Chemistry in the Ancona University, Italy. He is author or co-author of numerous papers on concrete technology and cement chemistry. He is also the recipient of awards for his contributions to the fundamental knowledge of superplasticizers and their use in concrete.

INTRODUCTION

The term Reactive Powder Concrete (*RPC*) has been used to describe a fiber-reinforced, superplasticized, silica fume-cement mixture with very low water-cement ratio (*w/c*) characterized by the presence of very fine quartz sand (0.15-0.40 mm) instead of ordinary aggregate (1, 2). In fact, it is not a concrete because there is no coarse aggregate in the cement mixture. The absence of coarse aggregate was considered by the inventors to be a key-aspect for the microstructure and the performance of the *RPC* (1, 2) in order to reduce the heterogeneity between the cement matrix and the aggregate. However, due to the use of very fine sand instead of ordinary aggregate, the cement factor of the *RPC* is as high as 900-1000 kg/m³. This unusual cement factor could increase drying-shrinkage and creep strain of the *RPC* with respect to ordinary concrete with cement factor usually in the range of 300-500 kg/m³.

The main purpose of the present investigation was to modify *RPC* including some coarse aggregate in the mixture and to study the influence of the coarse aggregate on the properties of cement mixtures in terms of required mixing water, compressive and flexural strength, shrinkage, swelling and creep.

Moreover, with respect to the original manufacturing process (1) - where additional sophisticated treatments are also used to remove the excess of mixing water through compacting pressure of the mixture in the moulds before and during setting, or to prolong the heating process at 90-400°C to dry the hardened material - traditional casting by vibration of fresh mixtures and conventional curing processes were adopted in the present investigation.

EXPERIMENTAL

Materials

A C₃A-free portland cement (Blaine fineness 340m²/kg), combined with a grey-coloured un-densified silica fume, was used as cementitious binder (Table 1). Details on chemical composition and properties of these materials were also given in previous papers (2, 3).

Fine ground quartz sand (0.15-0.40 mm) with a specific gravity of 2.75 g/cm³ was used for manufacturing the *RPC* mixture according to the original composition given by Richard and Cheyrezy (1). For modified *RPC* mixtures, well graded natural aggregate (maximum size: 8 mm, and specific gravity 2.75 g/cm³) was used to replace a part or the whole volume of the fine sand and/or a part of the cementitious binder. Figure 1 shows the particle size distribution of the ground fine sand in agreement with the original *RPC* and that of the natural aggregate - a limestone based rock - used in the present investigation to replace the fine sand and manufacture the *RPC*.

Steel fibers - 13 mm long with a diameter of 0.18 mm and an aspect ratio of 72 - were used.

An acrylic polymer (*AP*), in form of a 30% aqueous solution, was used as superplasticizer. Details on the performance of this superplasticizer, with respect to other superplasticizers, are given elsewhere (4, 5).

Concrete Mixtures

Three sets of concrete mixtures were manufactured with respect to the original *RPC* composition without coarse aggregate:

- i) a set where the amount of ground fine quartz sand (0.15-0.40 mm) of the original *RPC* composition was partially or totally replaced by the natural graded aggregate (0-8 mm) without changing the cement factor (Table 2);
- ii) a set where part of the cementitious binder (cement + silica fume) was replaced by the graded aggregate (0-8 mm) without changing the amount of fine sand (Table 3);
- iii) a set where part of the cementitious binder and the whole of fine sand was replaced by the graded aggregate (Table 4).

For each concrete mixture, a proper amount of mixing water - including that of the superplasticizer aqueous solution - was used to attain to the same workability level corresponding to a plastic-fluid consistency: 150-155 mm according to a modified flow table test described in other papers (2, 3).

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All concrete specimens were consolidated by vibration and measurements were carried out after an adequate curing time.

Curing

Concrete specimens were moist cured in three different conditions:

- a) *room temperature* (always at 20°C);
- b) *steam curing*: at 90°C after a preliminary curing at 20°C for 6 hours;
- c) *high-pressure steam curing* (autoclave process) at 160°C after a preliminary curing at 20°C for 24 hours.

Details of these curing process are shown in Fig. 2.

Measurements

The following properties were measured on hardened concrete specimens:

- compressive strength on cube specimens (40 mm);
- observation of the microstructure by scanning electron microscopy;
- flexural strength and stress-strain curves by symmetrical two point loading test on beam specimens (150x150x600 mm);
- flexural strength by one central loading test on prism specimens (40x40x160 mm);
- steel-concrete bond measured through pull-out test on deformed steel bars (diameter 20 mm) embedded for 100 mm in a 200-mm cube specimens;
- shrinkage (65% R.H.) and swelling (under water) of prism specimens (50x50x250 mm);
- modulus of elasticity and creep strain on cylinder specimens (diameter of 60 or 120 mm with height/diameter of 2) under stress of 13.3 or 53.0 MPa.

RESULTS

The data of the present work will be examined in two separate sections: preliminary tests on compressive strength of the mixtures shown in Tables 2 to 4, and the additional tests on some specific mixtures.

Compressive Strength

Figure 3 shows the compressive strength of the "original" *RPC* with ground quartz sand only (Mixture No. 1 on Table 2) versus modified *RPC* where this fine sand was partly or totally replaced by the graded aggregate with a maximum size of 8 mm. (Mixture No. 2 or 3 respectively). A small strength increase was recorded when the fine quartz sand (Mixture No. 1 in Fig. 4) was replaced by the coarser natural graded aggregate (Mixtures No. 2 and 3 in Fig. 4) due to the small reduction in the w/c (Table 2). The 28-day compressive strength was in the range of 160-180 MPa for the specimens cured at room temperature or steam-cured at 90°C, and in the range of 190-210 MPa for the autoclaved specimens cured at 160°C. Therefore, the compressive strength results of the present work do not confirm the beneficial role played by the very fine sand with respect to a coarser aggregate, as claimed by Richard and Cheyrezy (1, 2).

Figure 4 shows the effect of the graded natural aggregate, substituted for a part of portland cement and silica fume, on the compressive strength: due to reduction in the cementitious material, the w/c and $w/(c+sf)$ increased a little by using the graded aggregate (Table 3) and consequently the compressive strength of the modified *RPC* (Mixture No. 5 and 6 in Fig. 4) was a little lower with respect to the original one (Mixture No. 4 in Fig. 4).

Figure 5 shows the compressive strength of the modified *RPC* mixtures, all without very fine ground sand, and with reduced amounts of cement and silica fume (Mixtures 7, 8 and 9 of Table 4) with respect to that of the original *RPC* (Mixture No. 1, Table 2). Again, due to the increase in the water-cement and water-binder ratios (Tables 2 and 4), the compressive strength decreased by increasing the aggregate to cement ratio from 1.10 (original *RPC*) to 1.35-2.08 (modified *RPC*). However, the reduction in the compressive strength of the autoclaved specimens at 160°C was negligible with respect to that recorded for the specimens cured at lower temperatures (20°C or 90°C).

Additional Tests

Scanning electron micrographs. In order to understand the role played by the curing process in determining the performance of the material, the microstructure of *RPC* was studied by SEM. To facilitate the observation of the cement matrix, specimens without steel fibers were manufactured. Figure 6 shows typical fracture surfaces of *RPC* cured at 20°C, steam-cured at 90°C or autoclaved at 160°C. All specimens were observed at 7 days. The microstructure of the autoclaved specimen (Fig. 6C) was much more dense than that of the *RPC* steam-cured at 90°C (Fig. 6B) and this appeared a little less porous than the material cured at 20°C (Fig. 6A).

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Flexural strength. Table 5 shows the influence of the graded natural aggregate on the flexural strength with respect to the original *RPC* (Mixture No. 1); when all the fine ground sand was replaced by the coarser aggregate (Mixture No. 3) there was a reduction in strength and the effect was more significant when part of the cementitious binder and all the fine sand were replaced by the graded aggregate (Mixture No. 8).

Flexural strength, measured on larger specimen beams (150 mm thick) test through symmetrical two-point loading, were significantly lower than the values measured on smaller specimens (40-mm thick) by central point loading test. This agrees with the published data from technical literature (6). The flexural strength data (25-60 MPa) on *RPC* according to Richard and Cheyrezy (1) - obtained through central point loading test and relatively small specimens (40-70 mm) - are in good agreement with those of the present investigation of similar thickness (40 mm).

Bending stress-strain curves. Figure 7 shows the deflection of beams under bending stress for the original (Mixture No. 1) and modified *RPC* (Mixtures No. 3 and 8). A small change in the deflection curve is caused by replacing the fine ground sand of the original *RPC* (Mixture No. 1) with the graded aggregate (Mixture No. 3). A further reduction in the cementitious material (Mixture No. 8) reduced the area under the stress-deflection curve and therefore the toughness of the material.

Strength-bond. Table 5 shows that the steel-concrete bond, measured at 28 days on the specimens cured at 20°C, was much higher in modified *RPC* with coarse aggregate than in the original one. This could be ascribed to the interlocking between coarse aggregate and steel reinforcement which increases the stress required to pull the bar out.

Shrinkage-swelling behaviour. Original and modified *RPC* mixtures, after a 7 day curing time, were exposed to a 65% R.H. air for 30 days and then submerged under water (Fig. 9). In contrast with what happens for ordinary concretes, there was no significant change in the shrinkage-swelling behaviour as a function of the aggregate-cement ratio of the examined *RPC*. This can be ascribed to the very dense microstructure of the cement matrix of these materials. Moreover, both shrinkage and swelling, regardless of the mixture composition, were lower in steam-cured and specially in autoclaved specimens with respect to those cured at room temperature.

The shrinkage of original or modified *RPC* cured 7 days at room temperature was about $600 \cdot 10^{-6}$ after 1 month of air-exposure (65% R.H.). The change in dimensions of the autoclaved mixture was significantly lower - about 10 times less - than the corresponding material cured at room temperature. This is an agreement with both the microstructural densification produced by the autoclave curing at 160°C (Fig. 6) and the published data (6). On the other hand, the shrinkage reduction of the steam-cured (90°C) *RPC* with respect to that of the corresponding material cured at room temperature - less than 50% - is supported by the SEM observation of the present paper (Fig. 6), but it is not

confirmed by other published data (6). Nevertheless, some preliminary water absorption measurements - not shown in the present paper - indicated that steam-cured *RPC* at 90°C were less porous than the corresponding materials cured at room temperature and this could justify the differences in shrinkage and swelling as well between *RPC* cured at room temperature and that steam cured at 90°C.

Modulus of elasticity and creep behaviour. Figure 9 shows creep strains under permanent compressive stress of 13.3 or 53 MPa of the original *RPC* (Mixture No. 1) and modified *RPC* with the graded gravel replacing all the ground fine sand (Mixture No. 3) or substituting for part of the cementitious binder and all the fine sand (Mixture No. 8). All the specimens were steam-cured at 90°C and subjected to compressive loading at 7 days in the air (RH=65%), i.e. at a time when the compressive strength ranged from 150 to 160 MPa.

From the immediate strain of the specimens a modulus of elasticity of about 40 GPa was calculated for all the three mixtures and this value appeared to be lower than that recorded by Richard and Cheyrezy (56-60 GPa) for *RPC* with a compressive strength of 200 MPa (1).

The creep strain after loading of the *RPC* steam-cured specimens under the stress of 13.3 MPa (and therefore with a stress-strength ratio of about 0.09) was much lower than that of ordinary strength concrete with compressive strength of 30-40 MPa (6). The creep strain of the *RPC* specimens under the stress of 53 MPa (therefore with a stress-strength ratio of 1/3 at the loading time) was of course higher. However, the ultimate specific creep including the elastic strain was about $35 \cdot 10^{-6} \text{ MPa}^{-1}$ regardless of the stress-strength ratio and of the aggregate/cement ratio of the original or modified *RPC*, and then about one third of the specific creep of ordinary strength concrete (6).

Other creep tests indicated that the specific creep of autoclaved *RPC* was even lower, whereas that of *RPC* cured at room temperature was of the same order of magnitude as that of ordinary strength concretes.

CONCLUSIONS

The replacement of the fine ground quartz sand (0.15-0.40 mm) by an equal volume of well graded natural aggregate (maximum size: 8 mm) did not change the compressive strength of the *RPC* at the same water-cement ratio. These results are not in agreement with the model proposed by Richard and Cheyrezy since they attributed the high compressive strength level of *RPC* to a better homogeneity of the mixture in the absence of coarse aggregate.

When the graded aggregate replaced all the fine sand and part of the cementitious binder (cement and silica fume), at a given workability level, there

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was an increase in the water-cement ratio, due to the reduction in the cement factor, and hence a corresponding decrease in the compressive strength.

Flexural strength was lower when graded coarse aggregate replaced all the very fine sand. This effect could be explained in terms of a better homogeneity when only very fine sand is present and then to a more effective bond-strength between cement matrix and aggregate under shear stress produced in bending tests.

In the presence of coarse aggregate the steel-concrete bond was increased with respect of the original *RPC* and this effect could be ascribed to the interlock developing between coarse aggregate and deformed reinforcing bar.

Steam-curing at 90°C and specially high pressure steam-curing at 160°C gave a better performance of *RPC* - in terms of higher strength, lower drying shrinkage and creep strain - than the curing at room temperature. This improvement in the performance was related with a more densified microstructure of the cement matrix.

ACKNOWLEDGEMENT

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TABLE 1—COMPOSITION AND PROPERTIES OF SILICA FUME AND PORTLAND CEMENT (TYPE V ASTM OR CE I 42.5R ACCORDING TO ENV 197/1)

Composition (%) - Property	Portland Cement	Silica Fume
SiO ₂	20.59	98.87
Al ₂ O ₃	3.66	0.01
Fe ₂ O ₃	6.10	0.01
CaO	63.78	0.23
MgO	0.95	0.01
K ₂ O	0.48	0.08
Na ₂ O	0.26	0.00
SO ₃	250	0.23
C ₃ A	0	-
Blaine fineness (m ² /kg)	340	-
Mean particle size (μm): without superplasticizer	-	13.87
with superplasticizer	-	0.76

TABLE 2—COMPOSITION OF RPC MIXTURES WITH GRADED AGGREGATE (MAX SIZE = 8mm) REPLACING FINE SAND (0.15-0.40mm)

Mixture No.	1 (Original RPC)	2 (Modified RPC)	3 (Modified RPC)
Portland cement (<i>c</i>)	934 kg/m ³	933 kg/m ³	937 kg/m ³
Silica fume (<i>sf</i>)	234 kg/m ³	234 kg/m ³	235 kg/m ³
Fine sand (<i>fs</i>)	1030 kg/m ³	539 kg/m ³	—
Graded aggregate (<i>ga</i>)	—	489 kg/m ³	1031 kg/m ³
Superplasticizer (dry)	12.7 kg/m ³	12.7 kg/m ³	12.7 kg/m ³
Steel fibers	187 kg/m ³	187 kg/m ³	187 kg/m ³
water (<i>w</i>)	215 kg/m ³	205 kg/m ³	200 kg/m ³
<i>w/c</i>	0.23	0.22	0.21
<i>w/(c + sf)</i>	0.18	0.17	0.17
<i>fs/(fs + a)</i>	1.00	0.52	0.00
<i>a*/c</i>	1.10	1.10	1.10
Flow table (mm)	150	150	155

* *a* = total aggregate = *fs* + *ga*

TABLE 3—COMPOSITION OF RPC MIXTURES WITH GRADED AGGREGATE REPLACING PART OF THE CEMENTITIOUS BINDER (CEMENT + SILICA FUME)

Mixture No.	4 (Original RPC)	5 (Modified RPC)	6 (Modified RPC)
Portland cement (<i>c</i>)	934 kg/m ³	843 kg/m ³	754 kg/m ³
Silica fume (<i>sf</i>)	234 kg/m ³	211 kg/m ³	189 kg/m ³
Fine sand (<i>fs</i>)	1030 kg/m ³	1029 kg/m ³	1035 kg/m ³
Graded aggregate (<i>ga</i>)	—	109 kg/m ³	217 kg/m ³
Superplasticizer (dry)	12.7 kg/m ³	12.7 kg/m ³	12.8 kg/m ³
Steel fibers	187 kg/m ³	187 kg/m ³	188 kg/m ³
water (<i>w</i>)	215 kg/m ³	202 kg/m ³	204 kg/m ³
<i>w/c</i>	0.23	0.24	0.27
<i>w/(c + sf)</i>	0.18	0.19	0.22
<i>fs/(fs + a)</i>	1.00	0.90	0.82
<i>a*/c</i>	1.10	1.47	1.66
Flow table (mm)	150	150	155

* *a* = total aggregate = *fs* + *ga*

TABLE 4 —COMPOSITION OF RPC MIXTURES WITH GRADED AGGREGATE REPLACING ALL FINE SAND AND PART OF THE CEMENTITIOUS MATERIAL

Mixture No.	7 (Modified RPC)	8 (Modified RPC)	9 (Modified RPC)
Portland cement (<i>c</i>)	847 kg/m ³	758 kg/m ³	665 kg/m ³
Silica fume (<i>sf</i>)	212 kg/m ³	190 kg/m ³	166 kg/m ³
Graded aggregate (<i>ga</i>)	1146 kg/m ³	1259 kg/m ³	1383 kg/m ³
Steel fibers	188 kg/m ³	189 kg/m ³	189 kg/m ³
Superplasticizer (dry)	12.8 kg/m ³	12.9 kg/m ³	12.9 kg/m ³
water (<i>w</i>)	195 kg/m ³	192 kg/m ³	193 kg/m ³
<i>w/c</i>	0.23	0.25	0.29
<i>w/(c + sf)</i>	0.18	0.20	0.23
<i>a*/c</i>	1.35	1.66	2.08
Flow table (mm)	150	150	150

* *a* = total aggregate = *ga*

TABLE 5 — FLEXURAL STRENGTH: EFFECT OF REPLACEMENT OF THE CEMENTITIOUS BINDER (CEMENT + SILICA FUME AND FINE SAND BY THE GRADED AGGREGATE

Mixture No.	1	3	8
Portland cement (kg/m ³)	930	937	758
Silica fume (kg/m ³)	232	235	190
Fine sand (kg/m ³)	1024	-	-
Graded aggregate (kg/m ³)	-	1031	1259
w/c	0.22	0.21	0.25
Curing (max temperature)	20°C 90°C 160°C	20°C 90°C 160°C	20°C 90°C 160°C
Flexural strength (MPa) at	Two point loading tests on 150x150x600 mm beams		
- 3 days	16.7	17.8	18.2
- 7 days	19.6	21.9	18.1
- 28 days	20.5	20.1	18.0
Flexural strength at	Central point loading tests on 40x40x160 mm specimens		
- 3 days	39.6	30.7	30.2
- 7 days	43.8	34.9	36.8
- 28 days	45.7	35.5	38.3
Steel bond at 20°C (28 days)	28.4	37.9*	32.2*

* failure of the steel bar by tensile stress

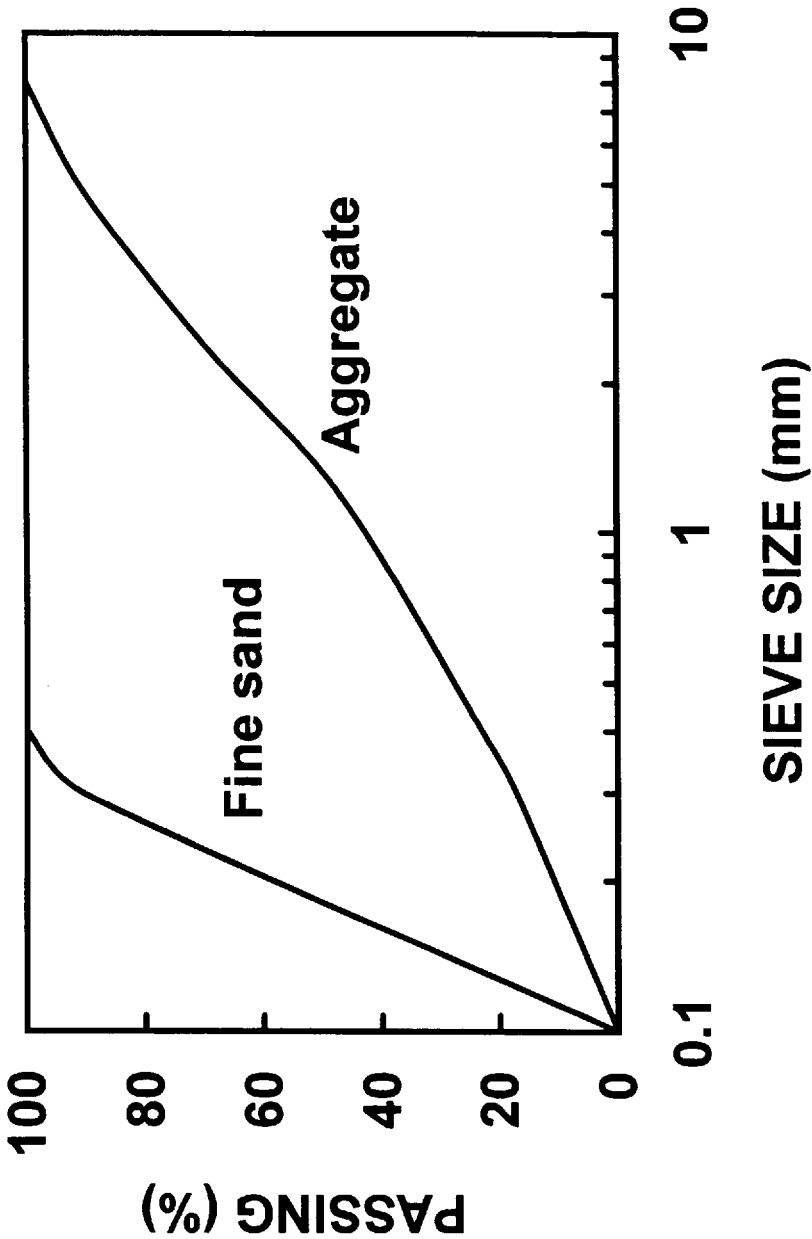


Fig. 1—Particle size distribution of the fine sand used in the original RPC and the aggregate used to replace it

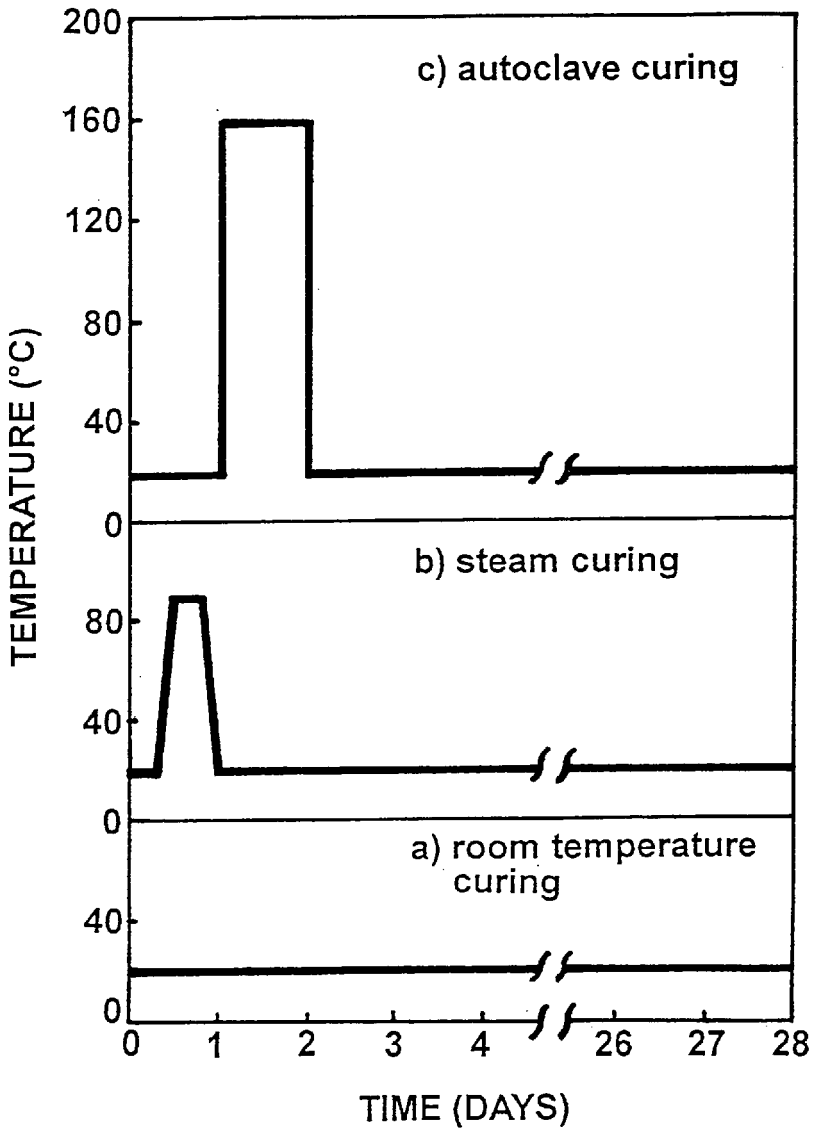


Fig. 2—Temperature versus time for the three curing conditions

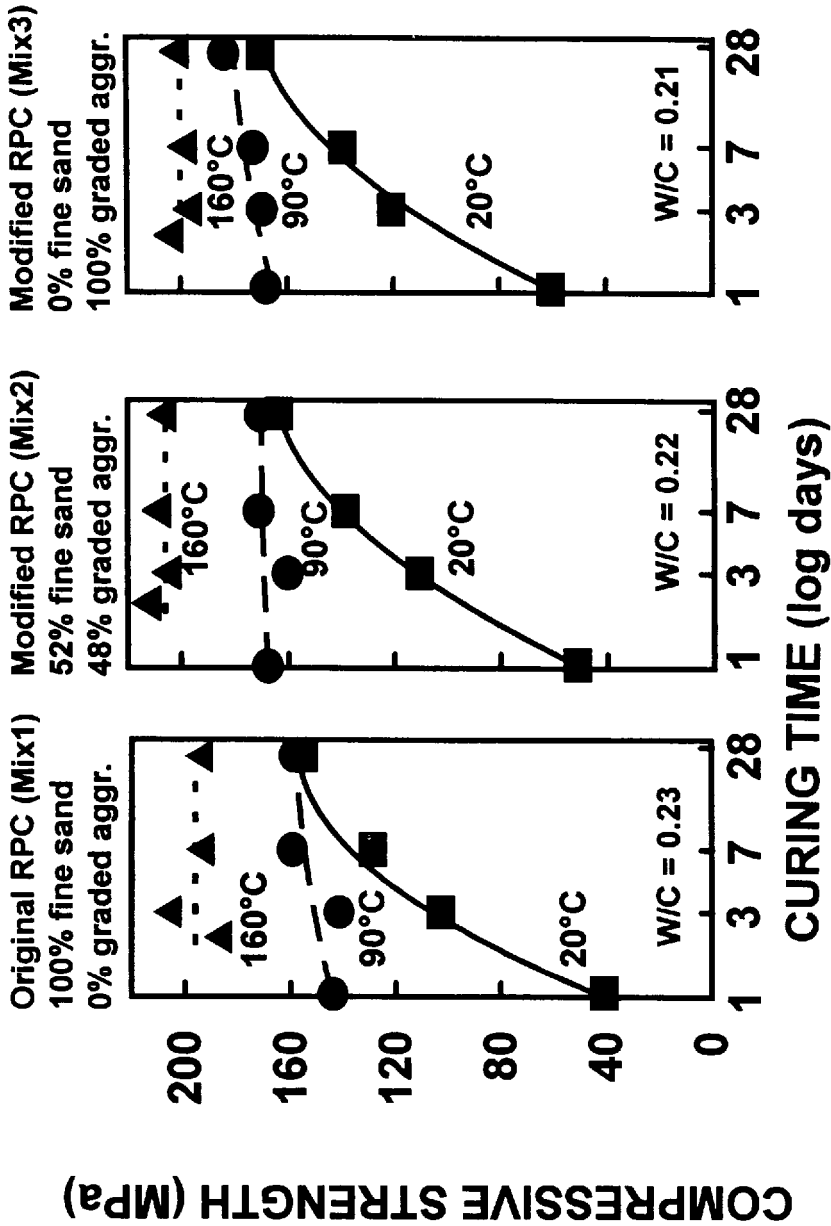


Fig. 3— Compressive strength versus curing time of mixtures 1, 2 and 3 (Table 2):
effect of replacement of fine sand by graded aggregate (0-8mm).

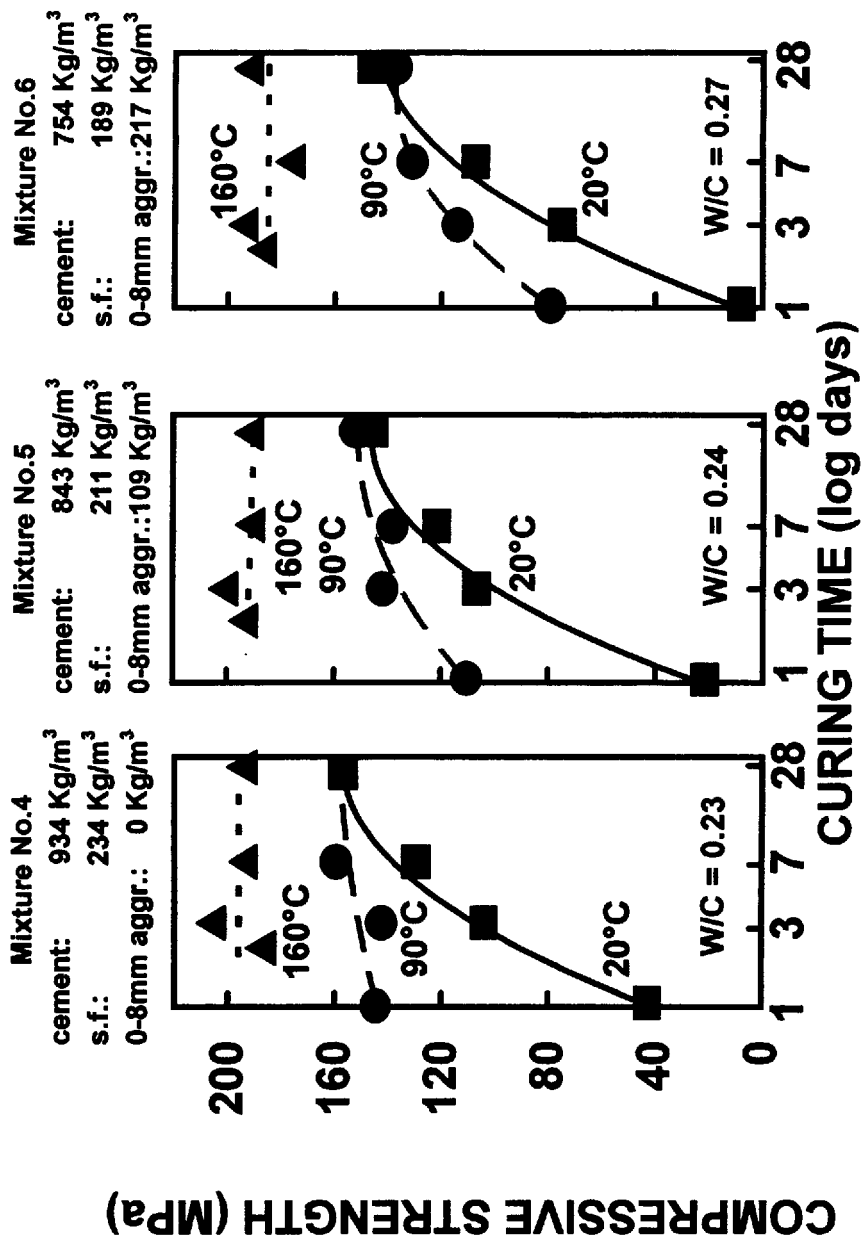


Fig. 4—Compressive strength versus curing time of mixtures 4,5 and 6 (Table 3): effect of replacement of cement, silica fume and fine sand by graded aggregate (0-8mm)

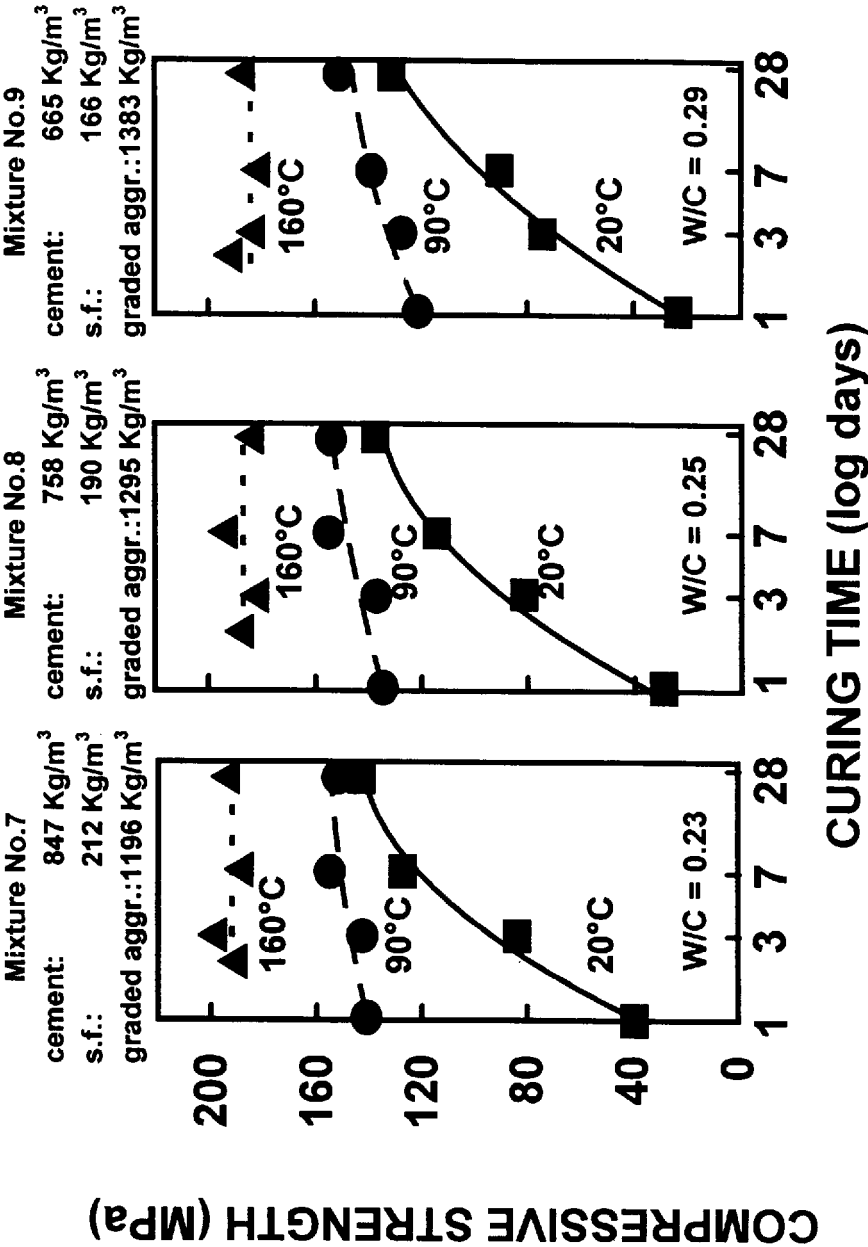


Fig. 5—Compressive strength versus curing time of mixtures 7,8 and 9 (Table 4): replacement of cementitious binder by the graded natural aggregate in the absence of fine-ground sand.

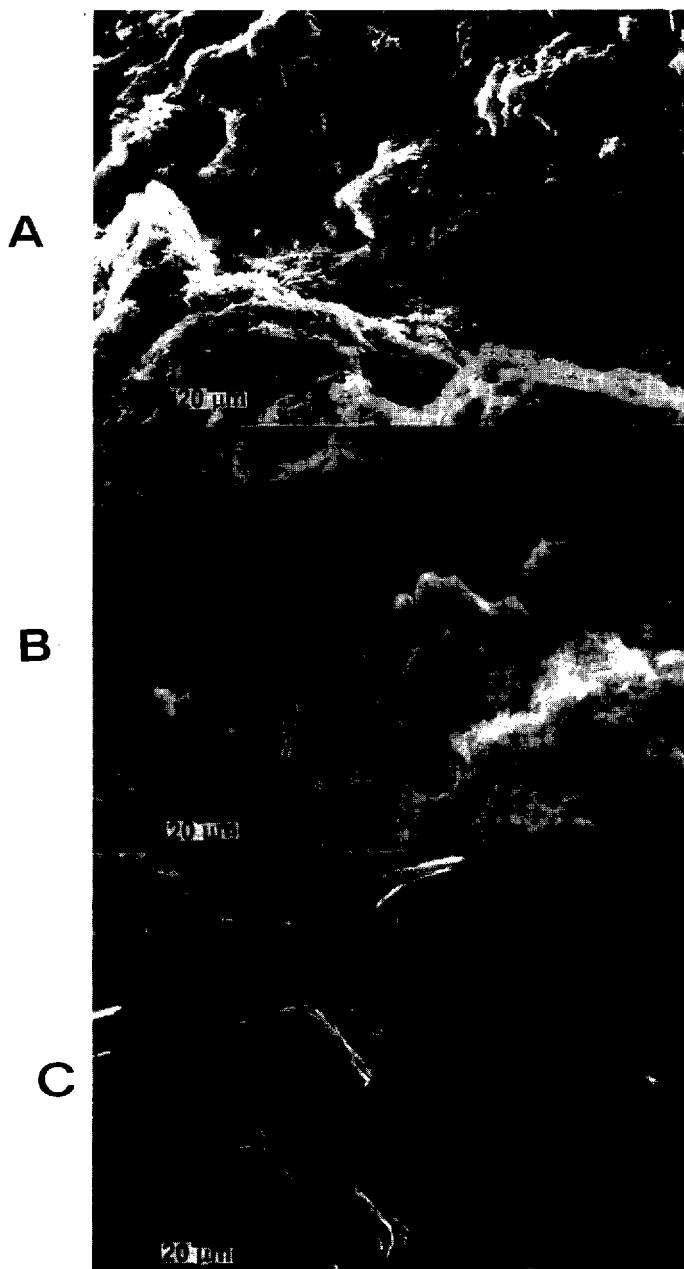


Fig. 6—Scanning electron micrographs of 7-day cured specimens in the absence of steel fibers. A: curing at 20°C; B: steam-curing at 90°C; C: autoclave curing at 160°C

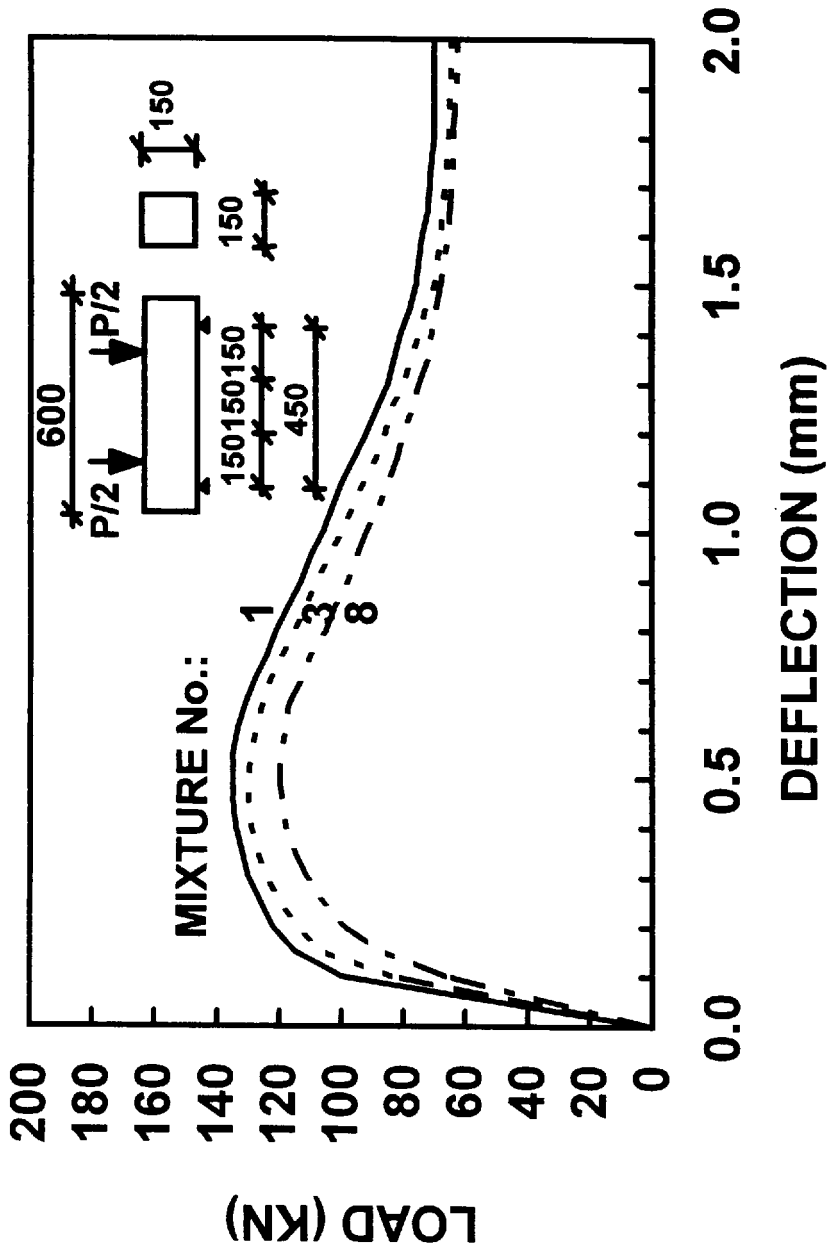


Fig. 7—Strain under flexural loading of steam-cured mixtures 1,3 and 8 (Tables 1 and 3) at 7 days

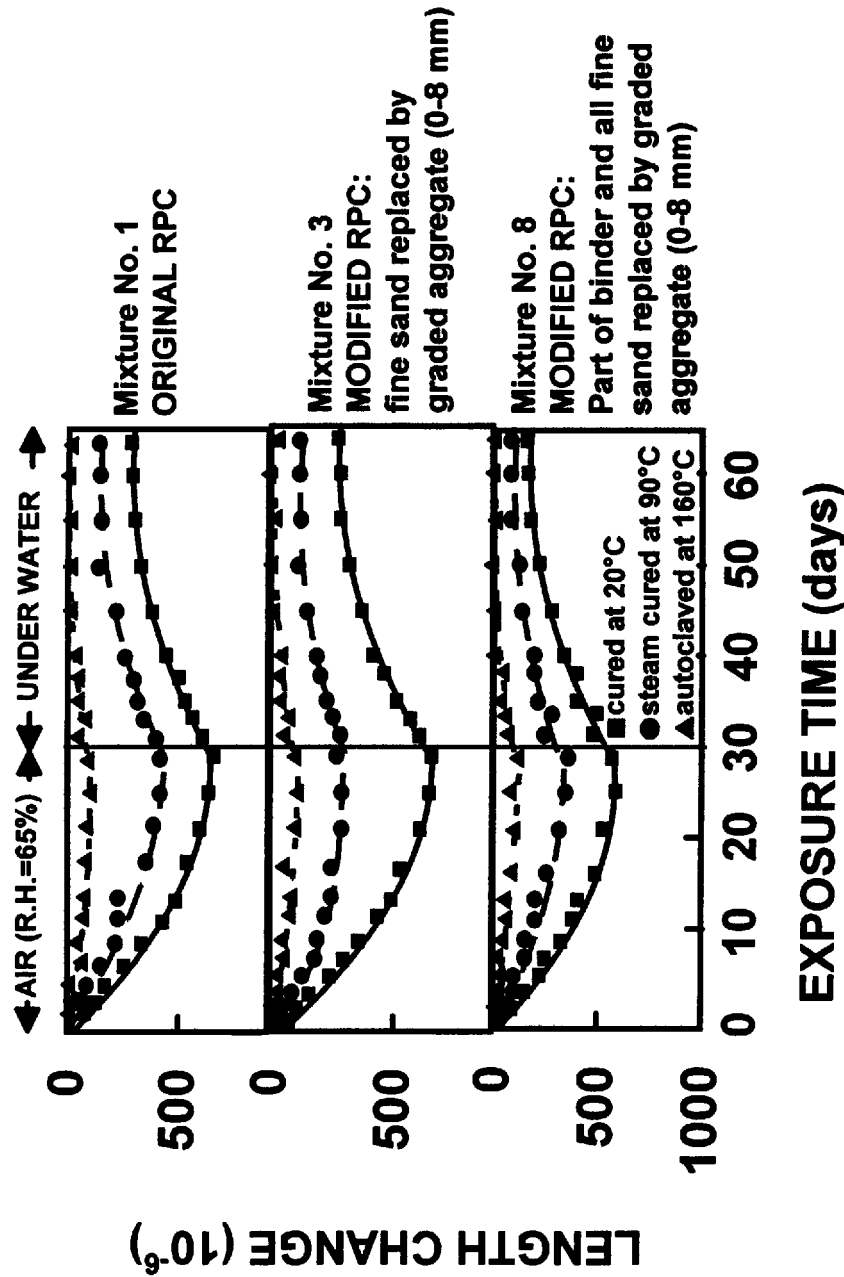


Fig. 8—Length change of specimens exposed to air and then to water after 7 days of curing

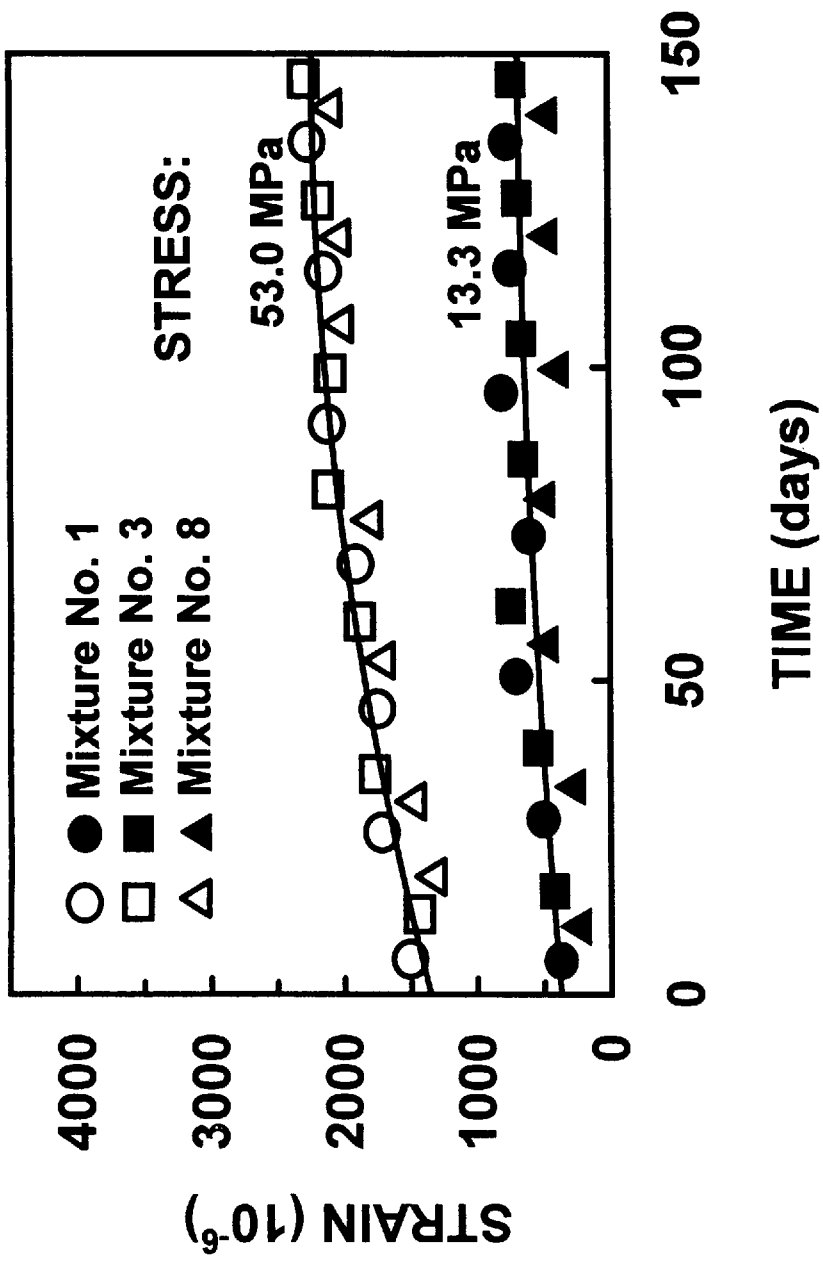


Fig. 9—Creep strain of concrete specimens steam-cured at 90°C and loaded at 7 days

Influence of Characteristics of Sulfonic Acid-Based Admixture on Interactive Force Between Cement Particles and Fluidity of Cement Paste

by Hiroshi Uchikawa and Shunsuke Hanehara

The relationships among the amounts of adsorption admixtures to cement particles, the interactive force between cement particles and the zeta potential of cement particle and the fluidity of cement paste prepared at the W/C ratio of 0.3 with lignin sulfonic acid-based admixture (LS), aminobenzene sulfonic acid-based admixture (AS) or melamine sulfonic acid-based admixture (MS) was studied in this paper, aiming at obtaining the basic data for elucidating the effects of the characters of sulfonic acid-based organic admixtures on the fluidity of concrete.

The amount of adsorption of the sulfonic acid-based admixture by cement particles are logarithmically related to the molecular weight of the admixtures. The lower the molecular weight, the more the amount adsorbed are. The zeta potential of cement particle in cement paste depends upon the content of sulfonate group in the admixture and the adsorption state of admixture. The interactive force between cement particles are linearly related to the fluidity of cement paste. The steric repulsive force considerably contributes to the dispersion of particles even in the addition of sulfonic acid-based admixture which has been considered so far to disperse the particles mainly by the electrostatic repulsive force. The steric repulsive force is related to the molecular weight of the sulfonic acid-based admixture except AS. The rate of contribution of electrostatic repulsive force to the total repulsive force accounting for the interactive force correlates with the content of sulfonate group in the admixture. The reason why the action of AS is different from those of the other admixtures is probably because the adsorption state of AS is different from those of the others.

Keywords: Admixtures; adsorption; cement pastes; forces

Hiroshi Uchikawa is Dr. Eng., P.E., Advisor to the President of Chichibu Onoda Cement Corporation and former Executive Director in charge of Research and Development of Onoda Cement Co. Ltd., Tokyo, Japan. He is also a Guest Professor of National Nagaoka University of Technology. He received several awards from domestic and international academic societies for his more than 40 years' sustained outstanding contribution to cement and concrete material science. He is the chairman and a member of several scientific committees of government and academic society and also the editorial board member of several international academic journals and a Fellow of American Ceramic Society.

Shunsuke Hanehara is Dr. Eng., a Manager of Central Research Laboratory, Chichibu Onoda Cement Corporation. He is an active member of the committee of cement chemistry of Japan Cement Association and the committee of autogenous shrinkage of Japan Concrete Institute.

INTRODUCTION

The existence of steric repulsive force has been invoked for by several researchers [1][2]. The steric repulsive force contributes to the solid particles in concrete prepared by adding a chemical admixture and contribution of the electrostatic repulsive force and sterical repulsive force in dispersions of cement particles and hydrates containing polycarboxylic acid-based admixture depend upon the types of it has been shown by the authors [3][4]. They have also reported that: 1) the thickness of the adsorbed layer of organic admixture to cement particles depends upon the kind of clinker mineral in such a way that the adsorbed layer on a C_3A is thick, while that on calcium silicate phase including a C_3S is thin; 2) the thickness of adsorbed layer and the degree of uneven adsorption depend upon the types of organic admixture; 3) the more the adsorption of organic admixture to the solid particles including cement, hydrates and blending component, the better the fluidity of the fresh cement paste and the lower the zeta potential (higher the absolute value), and 4) there is suitable molecular weight of the same series of organic admixtures composed of the same type of the main component to provide the best fluidity according the W/C ratio [2][5][6].

It has been considered so far that the sulfonic acid-based admixtures disperse the solid particles in concrete mainly by the electrostatic repulsive force, improve the fluidity of concrete and develop the water-reducing effect. Since the zeta potential measurements have however, become possible [3][4] under the conditions close to those in concrete, many experimental examples showing that the electrostatic repulsive force is not necessarily correlated with the fluidity of concrete have recently been reported [2].

This paper studies the relationships among the amounts of admixture adsorbed to cement particles, the interactive force between cement particles and the zeta potential of cement particle and the fluidity of cement paste prepared at the W/C ratio of 0.3 with lignin sulfonic acid-based admixture (LS), aminobenzene sulfonic acid-based admixture (AS) or melamine sulfonic acid-based admixture (MS) aiming at obtaining the basic data for elucidating the effects of the characters of sulfonic acid-based organic admixtures on the fluidity of concrete.

SAMPLE AND EXPERIMENTAL METHOD

Cement, Cement Clinker and Organic Admixture

Normal portland cement was used as shown in Table 1. Three types of sulfonic acid-based admixture were used as shown in Table 2. The solid contents of AS, LS and MS are from 22 to 49%. The maximum peaks in their molecular weight distributions are observed at 300, 35,000 and 78,000, respectively, and the degrees of condensation corresponding to their maximum peaks are 1, 120 and 270, respectively.

Preparation of Sample

Polished surfaces of cement clinker were used for measuring the interactive force between the surface of cement particles. The cement clinker samples were produced at the time when the cement as shown in Table 1 was manufactured. The cement clinker sample for measuring the interactive force is cut in a rectangular parallelepiped of 5mm x 5mm x 3mm with the cutter and the surface is carefully polished with corundum 0.05 μ m in diameter. Cement paste for measuring the zeta potential and flow were prepared at the W/C ratio of 0.3 by adding the admixture so as to make the weight ratio of the solid contents of admixture to cement 0.6%.

Measurement of Flow of Cement Paste

The value of flow of fresh cement paste was measured 10 minutes after the addition of mixing water with a flow cone for mortar test specified by JIS R5201.

Characterization of Admixture

Solid content, mean molecular weight and contents of sodium and Sulfur were determined according to the procedures described in [7]. The solid content in the admixture was determined from the weight after drying the liquid admixture at 110°C for one hour. The mean molecular weight was determined by gel permeation chromatography (GPC). The contents of sodium and sulfur are determined with a high-frequency inductively plasma emission spectrometry (ICP). The contents of carbon, hydrogen, oxygen and nitrogen are calculated from the structural formula of monomer of the admixture.

Measurement of Amount Adsorbed of Admixture

The amount of adsorbed admixture was measured using suspensions with a W/C of 5/1 prepared by adding the admixture so as to make the weight ratio of the solid content of admixture to cement 0.6%; the suspension was stirred in a constant temperature shaker at 20°C for 5 minutes, filtered by suction. The organic carbon remaining in the filtrate was determined with a total organic carbon analyzer (TOC-5000 manufactured by Shimadzu Co.) and the amount adsorbed was calculated by difference.

Measurement of Interactive Force between Cement Particles Adsorbing Admixture

The interactive force of cement particles adsorbing the admixture was determined with an atomic force microscope according to the procedure described in the previous papers [3][4]. A F-D curve of the admixture-adsorbing surface of the polished clinker immersed in an aqueous solution of the organic admixture for 5 minutes was determined to evaluate the force between the surfaces of cement particles adsorbing the admixtures. The reason why the immersion time in the aqueous solution of the organic admixture is fixed to 5 minutes is to prevent

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variation of the distance between the probe and the polished clinker surface by the dissolution of the components from the clinker and the deposition of hydrates on the polished surface [3][4]. Interactive forces measured in this paper were for cement clinker flat surface in the absence of SO_4^{2-} . It is considered, therefore, that in actual cement could markedly effect the absorption onto the cement clinker surface and the resulting potential. Auto Probe CP manufactured by Nikon/Park Scientific Instruments Co. was used as the AFM which uses a quadrangular silicon nitride probe of approximately 100 nm base length and a cantilever with the spring constant of 0.05 N/m. Prior to the measurement, the surface was carefully washed by UV ozone cleaning to remove the contaminants including organic matter until the surface was evenly wetted by water. The working range and speed of the cantilever were zero to 750 nm and 1,500 nm/sec, respectively.

Measurement of Zeta Potential of the Surface of Cement Particle Adsorbing Admixture

The zeta potential of the cement particle was determined 10 minutes after addition of mixing water to the cement paste prepared by the above-mentioned procedure with an electrokinetic sonic amplitude (ESA) method-zeta potential measuring apparatus (Acoustosizer manufactured by Matec Applied Sciences Co.). The ESA method is applied to the measurement of zeta potential in such a way that the electrokinetic sonic amplitude value (E) caused by the particles moving between both electrodes by applying higher frequency than 1MHz to the charged particles is measured, and zeta-potential is calculated with the value of E and the dynamic mobility of the particles. This method can accurately determine the zeta potential of the particle even in a suspension with high-concentration of solid unlike the conventional method such as electrophoretic method measures the migration speed of a dispersed particle in diluted suspension [3][4].

RESULTS AND DISCUSSION

Amount of Adsorption of Admixture

The amount of the sulfonic acid-based admixture of various types with low molecular weight several tens thousand or less adsorbed to the cement particles in fresh cement paste are logarithmically correlated with the molecular weight of admixture as illustrated in Fig. 1 in such a manner that the lower the molecular weight of admixture, the more the amount adsorbed of it is. The amount adsorbed corresponds to the product of the thickness and density of the adsorbed layer of admixture. The molecule with lower molecular weight has generally so larger polarization that makes higher-density multiple layers. The reason why the amount adsorbed of admixtures composed of low-molecular compounds are large is probably because of the phenomenon mentioned above.

Interactive force

The relationships between the distance from the surfaces of the adsorption layer of the admixtures determined from the F-D curve obtained 5 minutes after immersing the polished surface of cement clinker in various organic admixtures and the interactive force are illustrated in Fig. 2. The values obtained using pure water [3][4] is also shown in this figure for reference. Although the repulsive force on the polished surface of the clinker immersed in pure water was 0.004 nN, the maximum interactive forces on the polished surface of cement clinker immersed in an aqueous solutions of AS, LS and MS were 0.44nN, 0.16nN and 0.21nN, respectively. The operative distance of the repulsive force increased with increasing repulsive force due to the organic admixture. It was

approximately 10 nm for pure water, while approximately 420, 80 and 140 nm for the AS, LS and MS, respectively. The interactive force was increased by adding the admixture. The magnitude of this force is decreased in inverse proportion to the distance from the surface of the adsorption layer of admixture.

Zeta Potential of Cement Particle in Fresh Cement Paste

The zeta potentials of cement particles in fresh cement paste with the W/C of 0.3 prepared by adding AS, LS and MS were -9.9mV, -4.4mV and -7.7mV, respectively, while that prepared without admixture was -1.8mV. The zeta potential was decreased (absolute value increased) by adding the admixture.

Although negative charges result from the admixture by the dissociation of the sulfonate group are neutralized by adsorbing to the cement particles with positive potential, most of them remain intact and convey negative zeta potential to the cement particles. The zeta potential depends upon the content of sulfonate group and the extent of adsorption state of the admixture. When the adsorption states are the same as each other, therefore, the more the content of sulfonate group, the lower the zeta potential is (the higher the absolute value of it is).

Factors Affecting Fluidity of Fresh Cement Paste

The flow of fresh cement paste with the W/C of 0.3 prepared by adding AS, LS and MS were 324mm, 127mm and 176mm, respectively, while that prepared without adding the admixture was 113 mm. The flow is, therefore, sharply increased by adding the admixture.

The relationship between the zeta potential of cement particle in fresh cement paste prepared with and without the organic admixtures and the flow of fresh cement paste is illustrated in Fig. 3. The relationship between the interactive forces on the polished surface of cement clinker immersed in aqueous solutions of organic admixture measured by AFM and the flow of fresh cement paste is illustrated in Fig. 4.

The interactive force is linearly related to the flow of fresh cement paste independently of what types of admixture is added and whether the admixture is added or not. The flow is increased with the increase of the interactive force.

Since the measurements of the interactive force correspond to the sum total of the electrostatic repulsive force, steric repulsive force and van der Waals attraction of the surface of cement particles [3][4], the above-mentioned result is rational.

The flow of fresh cement paste is increased with the increase of the amount adsorption of admixture to cement particles described in the previous report [3][4]. Meanwhile the zeta potential is not necessarily related to the amount of adsorption of admixture, especially the relation was remarkably separated from the linear relation by adding AS.

This suggests that the force other than the zeta potential on the electrostatic repulsive force, relating to the amount of adsorption of admixture contributes to the improvement of the dispersion of cement particles, namely the fluidity of fresh cement paste.

Effects of Electrostatic and Steric Repulsive Forces on Fluidity

Since the van der Waals force is weak and short range, the sterically repulsive force as well as the electrostatic repulsive force are considered to contribute to the fluidity of cement paste. The steric repulsive force was obtained by subtracting the electrostatic repulsive force from force acting between cement particles, namely interactive force compensated from the interactive force measured by AFM according to the method described in the previous paper [3][4]. The relationship between the compensated interactive force of the surface of adsorbed layer of admixture and the distance, and that between the electrostatic repulsive force converted from the measured value of zeta potential referring the previous works [3][4][8] and the distance are illustrated in Fig. 5.

Although the electrostatic repulsive force contributing to the dispersion of cement particles in fresh cement paste without admixture is extremely small and the working region is also narrow, the force acting on the surface of cement particles is increased by adding the admixture. It is estimated, therefore, that the steric repulsive force contributes considerably to the dispersion of cement particles even in concrete prepared by adding the sulfonic acid-based admixture which is considered so far to contribute to the dispersion of solid particles such as cement mainly by the electrostatic repulsive force. The steric repulsive force is related to the molecular weight of the same series of admixtures excluding AS in case of the same adsorption state; the relative contribution of the electrostatic repulsive force to the total repulsive force of the same series of admixture is related to the ratio of functional group in the admixture. Although AS is low molecular weight because of low polymerization degree, the amount of adsorption to cement particles is large. Maybe this is because the adsorbed layer is thick and dense due to the multiple layer adsorption [5]. It was found that the interactive forces on the surfaces of cement particles adsorbing MS and LS are 0.21nN and 0.16nN, respectively, which were larger than values without adsorbed admixtures.

CONCLUSIONS

The conclusion obtained by investigating the influence of the characters of the sulfonic acid-based admixture on the interactive force between particles of cement in fresh cement paste and the fluidity are considered to be as follows:

- (1) The amount of adsorption of the sulfonic acid-based admixture by cement particles are logarithmically related to the molecular weight of the admixtures. The lower the molecular weight, the more the amount adsorbed.
- (2) The zeta potential of cement particle in cement paste depends upon the content of sulfonate group in the admixture and the adsorption state of admixture. The higher the content of sulfonate group in the admixture in the same adsorption state, the lower the zeta potential (higher absolute value).
- (3) The interactive force between cement particles are linearly related to the fluidity of cement paste.
- (4) The steric repulsive force contributes considerably to the dispersion of particles even in the addition of sulfonic acid-based admixtures which have been considered so far to disperse the particles mainly by the electrostatic repulsive force.
- (5) The steric repulsive force is related to the molecular weight of the sulfonic acid-based admixture except AS. The rate of contribution of electrostatic repulsive force to the total repulsive force accounting for the interactive force correlates with the content of sulfonate group in the admixture.

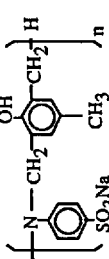
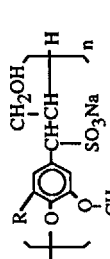
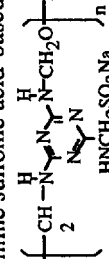
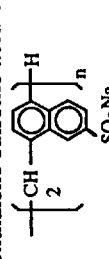
- (6) The reason why the action of AS is different from those of the other admixtures is probably because the adsorption state of AS is different from those of the others.

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TABLE 1—CHARACTER OF NORMAL PORTLAND CEMENT

Chemical composition (%)								Free lime (%)	Blaine specific surface area (cm ² /g)
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O		
22.1	5.3	3.1	65.2	1.2	2.1	0.43	0.23	0.5	3,350

Kind	Structural formula of main component	Solid Content	Molecular weight of unit monomer	Peak of molecular weight by GPC	Polymerization degree	C	H	O	N	SO ₃	Na
AS:	Aminobenzen sulfonic acid-based admixture 	44%	314	300	1	14	13	1	1	1	1
						53.5%	4.1%	5.1%	4.5%	25.6%	7.3%
LS:	Lignin sulfonic acid-based admixture 	49%	282	35000	124	10	11	3	0	1	1
						42.6%	3.9%	17.0%		28.4%	8.1%
MS:	Melamine sulfonic acid-based admixture 	22%	284	78000	275	6	9	1	6	1	1
						25.4%	3.2%	5.6%	29.6%	25.5%	9.2%
NS:	β-naphthalene sulfonic acid-based admixture 	40%	242	1560	6.5	11	7	0	0	1	1
						54.6%	2.9%			29.0%	7.2%

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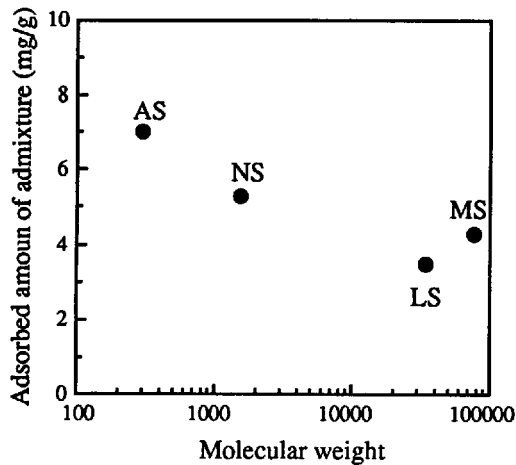


Fig. 1—Molecular weight and adsorbed amount of organic admixture, zeta potential and flow of fresh cement paste

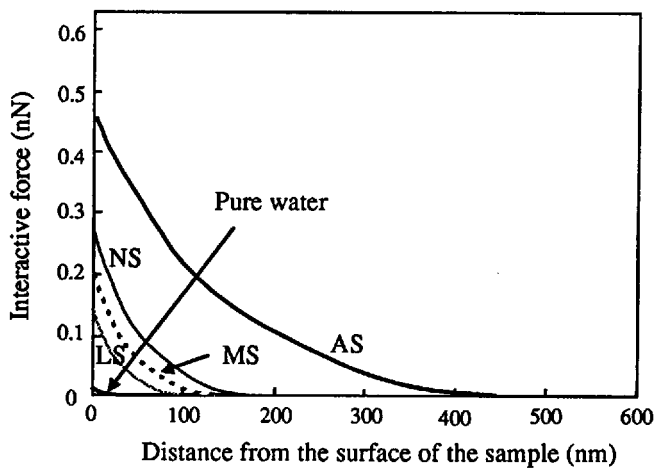


Fig. 2—relationship between interactive force and distance of polished cement clinker immersed in pure water and the 10% solutions of organic admixtures measured by AFM

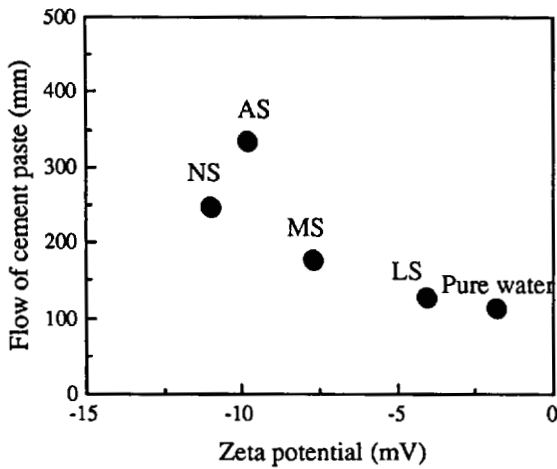


Fig. 3—Relationship between zeta potential and flow of fresh cement paste

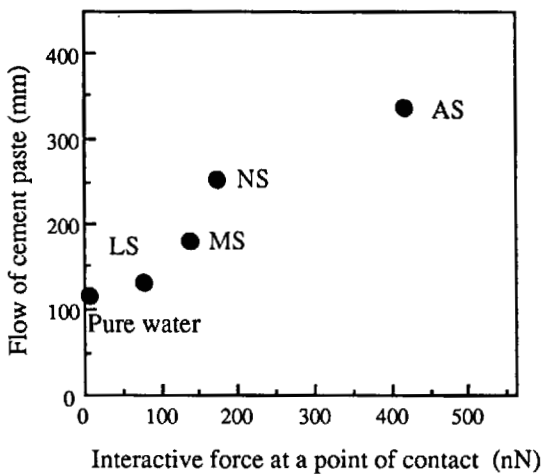


Fig. 4—Relationship between total repulsive force (interactive force) at a point of contact

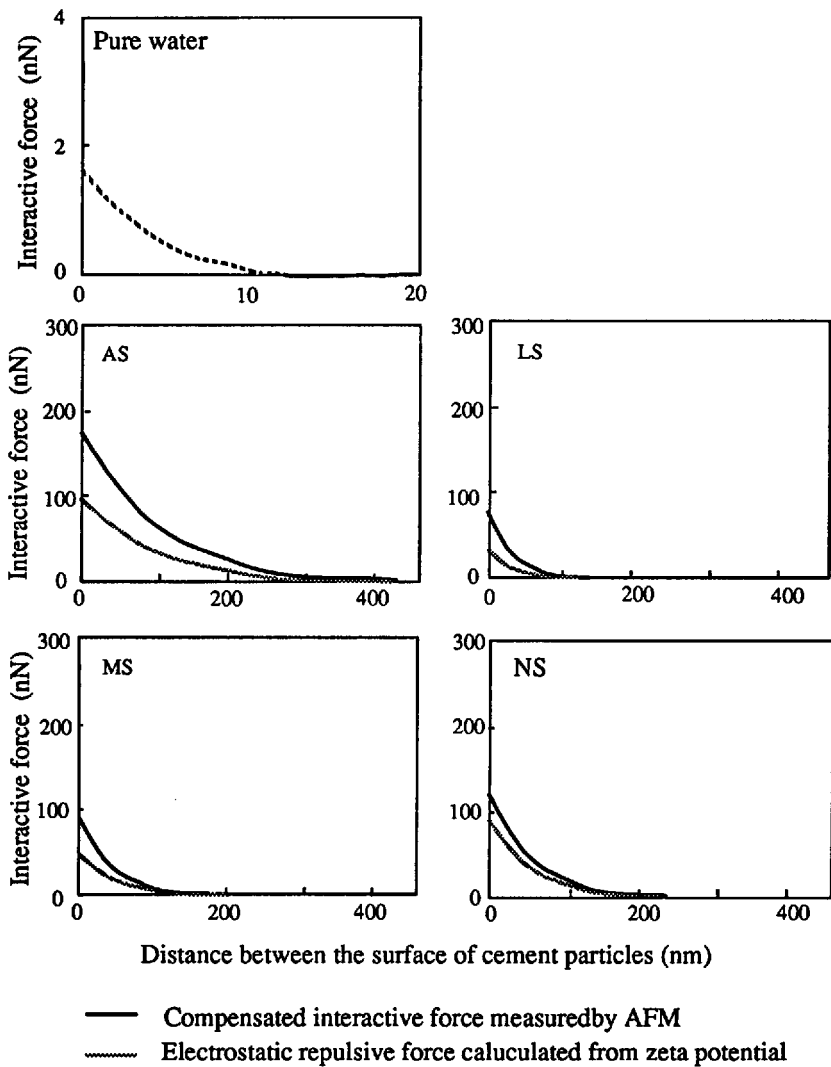


Fig. 5—The rate of contribution of electrostatic repulsive force working cement particle of $1\mu\text{m}$ in diameter

SP 173-3

Pore Solution Composition and Electrochemical Behavior of Steel Bars in Mortars with Nitrite Corrosion Inhibitors

by M. Kawamura, S. Tanikawa, R. N. Swamy
and H. Koto

Synopsis: The effectiveness of $\text{Ca}(\text{NO}_2)_2$ and NaNO_2 as corrosion inhibitors has been confirmed. However, the behavior of NO_2^- ion and its stability in the pore solution in concrete containing the inhibitors is a matter of concern for their effective use as a corrosion-inhibiting admixture. Furthermore, it may be important from the viewpoint of the corrosion of reinforcement in concretes contaminated with Cl^- ion to examine the behavior of NO_2^- ions in relation to Cl^- ion concentration in the pore solution in concrete. In this study, the analyses of pore solutions expressed from NaCl containing-mortars with and without the inhibitors were carried out to elucidate effects of the inhibitors on the chloride binding capacity of mortars. Simultaneously, the corrosion rate of steel bars embedded in the mortars was monitored by measurements of the potential and polarization resistance. The NO_2^- ion concentrations in the pore solutions in NaCl -containing mortars treated with 1% $\text{Ca}(\text{NO}_2)_2$ by mass of cement were lower than those in the corresponding mortars with NaNO_2 . The addition of NaNO_2 raised the OH^- ion concentration slightly, but the OH^- ion concentration was somewhat reduced in the mortars with $\text{Ca}(\text{NO}_2)_2$. The combined addition of NaCl and NaNO_2 , on the other hand, greatly raised the OH^- ion concentration. However, the $\text{Cl}^-/\text{NO}_2^-$ ratios in the pore solutions in mortars containing $\text{Ca}(\text{NO}_2)_2$ were slightly lower than in mortars containing NaNO_2 because of the dissipation of greater amounts of Cl^- ions from the pore solutions in the former than in the latter.

Keywords: Corrosion; nitrites; porosity; sands; sodium chloride; strength

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ACI member, Mitsunori Kawamura, is a professor in the Department of Civil Engineering at Kanazawa University, Japan. He has been active in cement and concrete research for about 30 years. His research interests include the alkali-silica reaction, concrete durability, and the microstructure of cement-based materials.

Shin Tanikawa is a Research Engineer with Toagosei Co. Ltd., Tokyo, Japan. He has carried out extensive research on concrete surface coatings. He is a student in the School of Natural Science, Kanazawa University.

ACI member, R. Narayan Swamy, is a professor at the Structural Integrity Research Institute, University of Sheffield, England. His research interests are in concrete materials and concrete structures. He received the CANMET/ACI Award for contribution to Durability of Concrete.

Hidefumi Koto is a Civil Engineer with Asanuma-Gumi Co. Ltd., Nagoya, Japan. He was a student in the School of Civil Engineering, Kanazawa University.

INTRODUCTION

Corrosion inhibitors have often been used in reinforced concrete when sea dredged sand has to be utilized as fine aggregate in order to avoid corrosion of the embedded steel reinforcement. $\text{Ca}(\text{NO}_2)_2$ and NaNO_2 have been investigated as inhibitors. The effectiveness of these inhibitors in the presence of chloride ions has been confirmed by investigating the electrochemical behavior of reinforcement in saturated $\text{Ca}(\text{OH})_2$ solution (1), the supernatant solution of cement (2), cement paste (3), mortars (4,5) and concrete (6). In these electrochemical studies, the threshold amount of the nitrites to be added for inhibiting corrosion of reinforcement has been discussed. The nitrite and chloride ion concentration in the pore solution is an important factor for the nitrites to function as an effective inhibitor. However, the behavior of nitrite and chloride ions in the pore solution in concrete and mortar containing NaCl and a nitrite has not been studied, and is not known.

In this study, on the assumption that the nitrite ions are used in concretes produced with a sea dredged sand contaminated with NaCl, time-dependent changes of the nitrite, chloride and hydroxide ion concentration in the pore solution of mortars containing both nitrite and NaCl have been investigated. In order to obtain a critical nitrite ion concentration for inhibiting corrosion of reinforcement, electrochemical measurements of mild steel electrodes embedded in mortars containing the nitrite and NaCl were made. The effects of the nitrite on the strength of mortars, and the alkali-silica reaction in concrete were also investigated.

EXPERIMENTAL PROGRAM

Materials

Reagent grade NaNO_2 and $\text{Ca}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ were used as corrosion inhibitors. A prescribed amount of reagent grade NaCl was added at the mixing stage of the mortars. The Japanese standard sand was used as a fine aggregate for producing mortars. The chemical composition of the cement used in the tests is given in Table 1.

Production and Curing of Mortar Test Specimens

The mortars specimens, 40 mm dia by 100 mm cylinders, from which the pore solutions were later expressed, were prepared with an aggregate:cement ratio of 2 and a water : cement ratio of 0.65. The amounts of chloride added to the mortar mixtures were 0.5% and 1.0% Cl^- by mass of cement. The dosage of NaNO_2 and $\text{Ca}(\text{NO}_2)_2$ was 1% by mass of cement. Mortar specimens without the nitrites and chlorides were also prepared as control specimens for comparison purposes.

For monitoring the electrochemical behavior of reinforcement, a mild steel electrode and a counter stainless steel electrode were embedded in beam specimen, 60 mm by 100 mm by 160 mm, which were made of the same mortars as above, as shown in Fig. 1. All the mortar cylinders were sealed in polyethylene sacks immediately after demoulding, and cured at 20° C and 95% R.H. for prescribed periods of time. The specimens, for making electrochemical measurements, in which the steel electrodes were embedded, were also stored in sealed polyethylene sack under the same environment as the mortar cylinders. The strength properties of the mortar mix were determined from 40 mm by 40 mm by 160 mm prisms according to Japanese Standard JIS R 5201.

Pore Solution Analysis and Electrochemical Measurements

After curing for prescribed periods, pore solutions were extracted from mortar cylinders by a high-pressure apparatus similar to that described by Barneyback and Diamond (7). The Na^+ , K^+ and Ca^{2+} ion concentrations were determined by atomic absorption analysis, the OH^- ion concentrations by titration with HCl , and SO_4^{2-} and Cl^- ion concentrations by ion chromatography. No adjustment for reduction in water content through progressive hydration was made. The pore solution analysis tests were carried out up to 90 days.

Corrosion intensities of the steel electrodes were evaluated by polarization resistance measurements. A potential scan, 20 mV either side of the rest potential was applied at 10 mV/min., and the potential (E)-current(I) curves were recorded. The saturated calomel half-cell was used as a reference electrode. The polarization resistance, $\Delta E/\Delta I$, was calculated from the slope of the measured polarization curve. In this study, the inverse of the polarization resistance was used as a measure of the relative corrosion rate. Measurements were made on duplicate specimens once a week. All the electrochemical tests were carried out for 300 days.

Flexural and Compressive Strength of Mortar

Flexural and compressive strength tests were carried out at different ages up to 90 days according to JIS R 5201 with mortar prisms, 40 mm by 40 mm by 160 mm size.

TEST RESULTS AND DISCUSSION

Changes in Ion Concentration with Time

The Na^+ , K^+ , Ca^{2+} , OH^- , Cl^- , NO_2^- and SO_4^{2-} ion concentrations of pore solutions extracted from mortars with and without chlorides and nitrites are tabulated in Table 2. The balance in concentration between cations and anions was good. The Cl^-/OH^- and $\text{Cl}^-/\text{NO}_2^-$ ion concentration ratios are also given in Table 2.

Pore Solution Composition in Mortars without Nitrite--Fig. 2 shows changes in the anion concentration with time in mortars without nitrite. The OH^- ion concentration in both mortars with a Cl^- ion concentration of 0.5% and 1.0% rapidly increased with time for a period of 1 to 7 days, as reported earlier by Kawamura et al. (8), and then increased at a very slow rate. The OH^- ion concentration may have risen in part due to the formation of calcium chloroaluminate, the amount of which increased with increasing amount of added Cl^- ions. Naturally, a part of the increase in the OH^- ion concentration may have been caused by a reduction in the water content through progress of cement hydration. Unlike the OH^- ion concentrations, the Cl^- ion concentration was very high initially, but it decreased very rapidly and remained thereafter more or less constant for the whole test period of 90 days. The extent of reduction in Cl^- ion concentration for the period of 1 to 90 days in the mortars with added 1.0% Cl^- ion was found to be about twice that in the mortars with added 0.5% Cl^- ion. This shows that the amount of C_3A in the cement was high enough for at least 1% Cl^- ion to be fixed as chloroaluminate.

Pore Solution Composition in Mortars with NaNO_2 --Plots of the concentration of various anions in the pore solution in mortars with NaNO_2 at various ages are given in Fig. 3. It is found by comparison between the data for mortars without NaCl in Figs. 2 and 3 that the addition of NaNO_2 raised the OH^- ion concentration in the pore solutions. The addition of both NaNO_2 and NaCl in mortar also increased the OH^- ion concentration up to 0.64 M. This result suggests that the use of NaNO_2 as an inhibitor in concrete produced with an aggregate contaminated with NaCl would significantly increase the possibility of deterioration of concrete due to the alkali-silica reaction. A comparison of Cl^- ion concentration between the mortars with and without NaNO_2 at a Cl^- content level of 1.0% (Figs. 2 and 3) shows that the addition of NaNO_2 increased slightly the Cl^- ion concentration in the pore solutions. This result indicates that the incorporation of NaNO_2 as an inhibitor reduces slightly the binding capacity of the chlorides in mortar. On the contrary, as shown in Fig. 3, the eventual NO_2^- ion concentration in the pore solution also increased with increasing chloride ion content of the mortar. The presence of the chloride appears to hinder NO_2^- ions from being fixed into the hydration products.

Pore Solution Composition in Mortars with $\text{Ca}(\text{NO}_2)_2$ --Fig. 4 shows the time-dependent changes in the concentration of various ions in the pore solutions in mortars with $\text{Ca}(\text{NO}_2)_2$. The OH^- ion concentrations are found to be reduced by the addition of $\text{Ca}(\text{NO}_2)_2$ (Figs.2 and 4). However, the OH^- ion concentration in mortars with $\text{Ca}(\text{NO}_2)_2$ was raised by the presence of NaCl . On the other hand, it should be noted that the Cl^- ion concentrations in mortars with $\text{Ca}(\text{NO}_2)_2$ were significantly lower than those in mortars with NaNO_2 . The NO_2^- ion concentrations in mortars with $\text{Ca}(\text{NO}_2)_2$ were also slightly lower than those in mortars with NaNO_2 .

Cl^-/OH^- and $\text{Cl}^-/\text{NO}_2^-$ Ion Concentration Ratio--In order to evaluate the effectiveness of the nitrites as an inhibitor, the Cl^-/OH^- and $\text{Cl}^-/\text{NO}_2^-$ ratios in the pore solutions in the mortars with the nitrites were plotted against time, as shown in Figs. 5 and 6. It is found from Fig. 5 that the differences in Cl^-/OH^- ratio and $\text{Cl}^-/\text{NO}_2^-$ ratio between different mortars with 0.5% Cl^- addition are very small. However, the $\text{Cl}^-/\text{NO}_2^-$ ratios in mortars with a Cl^- ion content of 1.0% were considerably higher than those in mortars with a Cl^- ion content of 0.5%. Furthermore, at a Cl^- ion content of 1.0%, the $\text{Cl}^-/\text{NO}_2^-$ ratios in mortars with $\text{Ca}(\text{NO}_2)_2$ were considerably lower than in mortars with NaNO_2 . These results suggest that with high chloride concentration $\text{Ca}(\text{NO}_2)_2$ is more effective as an inhibitor than NaNO_2 .

Effects of the Nitrites on Strength

The data concerning the effects of the nitrites on flexural strength are given in Fig. 7. In mortars without chlorides, and in mortars at 0.5% Cl^- content, the addition of sodium nitrite enhanced the flexural strength up to 7 days. However, with aging this strength increase with sodium nitrite was reversed, and the strength at 90 days of mortars with nitrite was lower than those of mortars without nitrite. At the age of 90 days the flexural strength of mortars with sodium nitrite was by about 15% lower than those of mortars without sodium nitrite. This was also the case at a Cl^- ion content of 1% except that there was no early strength increase at 7 days at this Cl^- content level. On average, there were only minor differences in the flexural strength of mortars with NaNO_2 and $\text{Ca}(\text{NO}_2)_2$ at all chloride content levels.

Fig. 8 shows the changes in the compressive strength with time of mortars with and without nitrite. The compressive strength at 90 days of mortars with Cl^- ion contents of 0, 0.5% and 1.0% was reduced by about 18%, 15% and 13%, respectively, on average, when a nitrite was added. Differences in compressive strength between mortars with NaNO_2 and $\text{Ca}(\text{NO}_2)_2$ were generally small, although sodium nitrite always consistently gave lower strengths than calcium nitrite.

Electrochemical Behavior of Embedded Steel Electrode

Figs. 9 and 10 respectively show the time-dependent changes of the corrosion potential and the relative corrosion rate (the inverse of the polarization resistance) of steel bars embedded in mortars with and without nitrite.

Steel Bar in Mortars without Nitrite--As shown in Fig. 9 (a), in mortars without chlorides, the corrosion potential of the steel electrode was maintained

around -100 mV, which is indicative of passive conditions (9). In mortar with a Cl^- ion content of 0.5%, the corrosion potential initially started at about -440 mV, which is indicative of active corrosion (9). However, the potential rapidly changed, reaching steady level of about -250 mV which corresponds to a reduced level of corrosion. These changes in electrochemical behavior are considered to be in response to the changes of the Cl^-/OH^- ratio in the pore solution with time. As shown in Figs. 5 and 9 (a), the rapid reduction of the potential at the early stages corresponds to the evolution of pore solutions with high Cl^-/OH^- ratios. As the Cl^-/OH^- ratio decreased with time, the potential increased thereby reducing the risk of corrosion. The trend of time-dependent changes in the potential in mortars with a Cl^- ion content of 1.0% was similar, up to about 200 days, to that in mortars with a Cl^- ion content of 0.5%. At this chloride content, the potential reached a steady value of -330 mV, but after about 200 days, the potential reduced further to a steady value of -200 mV. Obviously, at this potential, the risk of further corrosion is reduced. The precise reasons for these changes are not clear at the moment. The relative corrosion rates shown in Fig. 10 (a) for the nitrite-free mortars correspond well with the potential changes shown in Fig. 9 (a). As shown in Fig. 10, the relative corrosion rates of steel bar embedded in the chloride-free mortar were extremely low. The steel bar in the mortar with a Cl^- ion content of 0.5% showed a high corrosion rate on the first day, but this was followed by a rapid reduction leading to the steady state of a relatively low corrosion rate. In the mortar with a Cl^- ion content of 1.0%, a great reduction in the corrosion rate of the steel bar also occurred during the first day. Even then, a relatively high level of corrosion rate resulted, and this was maintained up to about 200 days when there was a still further reduction in corrosion rate to negligible levels, confirming the changes in electropotential shown in Fig. 9 (a).

Steel Bar in Mortars with NaNO_2 —The potentials of about -185 mV measured for the NaNO_2 -containing mortar with a Cl^- content of 0.5% during the period of 1 to 175 days (Fig. 9 (b)) show that the addition of 1% NaNO_2 to the mortar with a Cl^- ion content of 0.5% was effective in keeping the steel bar inconclusive state as regards corrosion. However, there was a clear trend of increasing negative potential after 200 days, emphasizing the possibility of risk of corrosion with time. This is confirmed by the corrosion rates results shown in Fig. 10 (b), which shows an extremely low corrosion rate up to about 170 days, after which there is a evidence of slightly increasing corrosion rate. At a Cl^- ion content of 1.0%, a low potential of about -380 mV was maintained for the period of 7 to about 180 days. This is confirmed by the corrosion rate shown in Fig. 10 (b); at about 200 days, the electropotential was reduced indicating a lowering of the corrosion rate. In general terms, the presence of sodium nitrite reduced the rate of corrosion initially up to about 200 days compared to the mortar without the nitrite; however, there was clear indication of increased corrosion activity in mortars with 1% NaCl .

Steel Bar in Mortars with $\text{Ca}(\text{NO}_2)_2$ —As shown in Fig. 9, the electropotential of the bar in the mortar with a Cl^- ion content of 0.5% was almost the same as that of the bar in the reference mortar up to at least about 300 days. However, an increase in Cl^- ion content to 1.0% increased the potential to the level of about -300 mV. Accordingly, there was a modest, but progressively increasing corrosion current in the steel bar in the mortar, although the corrosion rate was actually zero in the mortar without Cl^- ion.