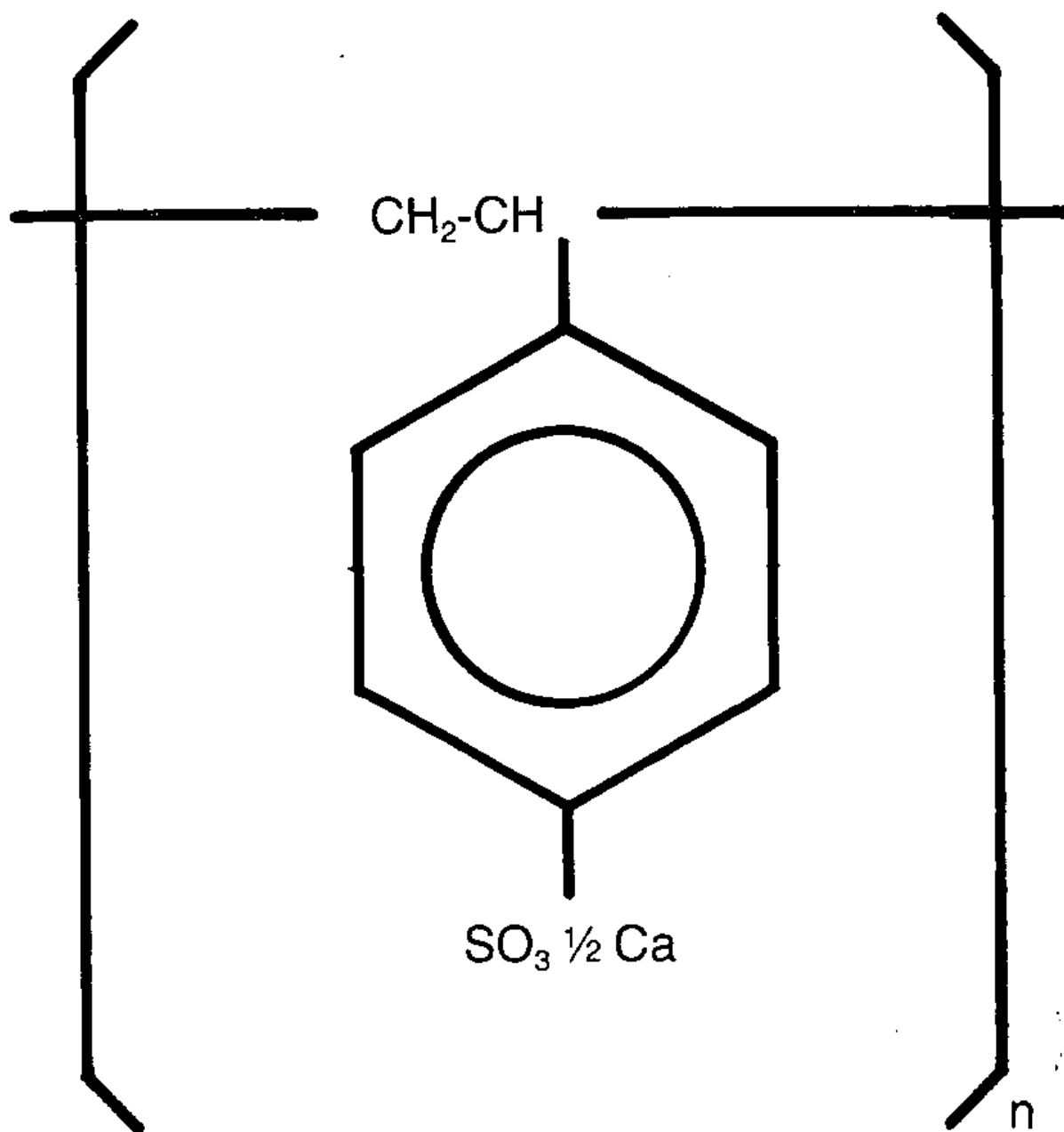


# Superplasticizers and Other Chemical Admixtures in Concrete

Proceedings Third International Conference  
Ottawa, Canada, 1989



American Concrete Institute, Detroit

V.M. Malhotra  
*Editor*



SP-119

# Optimization of Superplasticizer Type And Dosage in Fly Ash And Silica Fume Concretes

by M. Collepari, S. Monosi, and M. Valente

Synopsis: The purpose of the present work was to optimize the type and the dosage of superplasticizer in concretes incorporating ASTM Class F fly ash, so that compressive strengths as high as those of superplasticized silica fume concretes could be obtained.

Two types of high-range water reducers based on Sulfonated Naphtalene Polymer (SNP) and Sulfonated Melamine Polymer (SMP) - both as 40% aqueous solution - have been used in the presence of fly ash or silica fume to manufacture superplasticized flowing concretes containing ASTM Type I or Type III portland cements. The superplasticizer dosage and the pozzolan addition ranged from 2 to 4% and from 12 to 20% respectively by weight of cement. The cement factor varied from 255 to 400 kg/m<sup>3</sup>.

The results of the investigation work indicate that only in the presence of ASTM Type III portland cement, superplasticized fly ash concrete can be as strong as the corresponding silica fume concrete, particularly at relatively high cement factors ( $\geq 300$  kg/m<sup>3</sup>).

Keywords: compressive strength; concretes; fly ash; optimization; plasticizers; portland cements; silica fume

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### INTRODUCTION

Silica fume is generally used in combination with a superplasticizer to manufacture high-strength concretes, whereas fly ash with or without plasticizer or superplasticizer is generally devoted to ordinary-strength concretes (1, 2, 3).

The silica fume is considered generally to be more efficient as a pozzolan than fly ash. The purpose of the present research was to find out if superplasticized fly ash concretes could be manufactured with compressive strength as high as those of superplasticized silica fume concretes. This could be very important from a practical point of view, since silica fume is much more expensive and less available than fly ash.

### EXPERIMENTAL PROGRAM

Sixty-four different concrete mixes (Tables 1 to 8) were made with silica fume or ASTM Class F fly ash by using portland cement ASTM types I and III. The cement factors ranged from 255 to 400 kg/m<sup>3</sup> and the superplasticizers used were Sulphonated Naphtalene Polymer (SNP) and Sulphonated Melamine Polymer (SMP). The dosage of the superplasticizer ranged from 2 to 4% by weight of cement.

All the concrete mixes were produced at a flowable consistency (slump of 220 +/- 10 mm). The sand, with a fineness

modulus of 2.65, was 40% of the total weight of limestone aggregates, and the maximum size of the coarse aggregate was 25 mm. The silica fume and fly ash content was nominally 60 kg/m<sup>3</sup> in richer cement mixes (340 and 400 kg/m<sup>3</sup>), and 45 kg/m<sup>3</sup> in leaner ones (255 and 300 kg/m<sup>3</sup>). In some cases (nominal cement content of 300 kg/m<sup>3</sup>) the air content of fresh concretes was measured (Table 2 and 6).

Table 9 indicates chemical and physical characteristics of silica fume, fly ash and portland cements used.

Superplasticizers based on a 40% aqueous solution of SNP or SMP, both produced by MAC-MBT as Rheobuild 2000 or Rheobuild 2000 B respectively, have been used. Compressive strengths on 150 mm cube specimens cured at 20°C and 95% R.H. have been measured at 1, 7 and 28 days.

#### TEST RESULTS AND DISCUSSIONS

As the effect of silica fume or fly ash on concrete compressive strength depend on the Portland cement type, the results of the present work will be examined in two separate sections, a and b, concerning ASTM Type I and Type III portland cement respectively.

##### a) ASTM Type I Portland Cement Mixes

Figures 1, 2, 3 and 4 indicate the compressive strength of concretes at a nominal cement factor of 255, 300, 340 and 400 kg/m<sup>3</sup> respectively.

Superplasticized silica fume concretes are stronger than the corresponding fly ash concretes particularly at later ages ( $\geq 7$  days) and with lower cement factors (260-300 kg/m<sup>3</sup>).

In silica fume concretes at 4% dosage, the melamine polymer appears to be more effective than the naphtalene one as far as the strength increase is concerned, whereas no substantial difference in strength performances between the two polymers can be found at 2% dosage. The increase in strength cannot be related to a reduction in the water/cement ratio, since the melamine

polymer as a water reducer, appears to be less effective than the naphthalene one particularly at 2% dosage (Tables 1 to 4). The naphthalene polymer appears to be more retarding on cement hydration than the melamine polymer, particularly when a relatively high dosage (4%) is used.

In fly ash concrete there is no significant difference in strength performances between the melamine polymer and the naphthalene one independently of the dosage, even if the naphthalene polymer, as water reducer (Tables 1 to 4), appears to be more effective than the melamine one. Again, it seems that there is a retarding action of the SNP polymer on cement hydration particularly in the presence of fly ash.

In silica fume concretes, by increasing the dosage from 2 to 4%, there is a significant strength increase independently of the polymer type. It seems that the retarding action of SNP at relatively high dosage is reduced in the presence of silica fume.

In fly ash concretes, by increasing the superplasticizer dosage from 2 to 4%, in general there is a small reduction in strength, particularly in lean mixes although the water/cement ratio is significantly reduced (Tables 1 to 4). Only in richer mixes ( $\geq 340 \text{ kg/m}^3$ ) and later ages ( $\geq 7$  days) there is a small strength increase.

Only at the higher dosage of superplasticizer (4%) the air content of SNP concretes is higher than that of SMP mixes independently of the presence of fly ash or silica fume (Table 2). This could explain why the difference between strengths of SMP and SNP concretes is higher at the higher superplasticizer dosage.

#### b) Type III Portland Cement Mixes

Figures 5, 6, 7 and 8 indicate the compressive strength of concretes containing Type III portland cement at a nominal cement factor of 255, 300, 340 and  $400 \text{ kg/m}^3$ .

Superplasticized fly ash concretes are as strong as those containing silica fume and superplasticizer, particularly at relatively high cement factors ( $\geq 300 \text{ kg/m}^3$ ); in leaner cement mixes silica fume performs a little better than fly ash.

At superplasticizer dosage of 2% SMP performs as well as SNP in the presence of fly ash or silica fume, even if SNP is more effective as water reducer (Tables 5 to 8); at higher dosage, such as 4%, the SMP superplasticizer performs better than the SNP in the presence of silica fume or fly ash although the water reduction effect of the two polymers is substantially the same. This would indicate a certain retarding effect of SNP on the cement hydration.

By increasing the superplasticizer dosage from 2 to 4%, the compressive strength of both silica fume and fly ash concretes is increased independently of the polymer type. Therefore the retarding action of SNP at relatively high dosage (4%) appears to be reduced when ASTM Type III portland cement is used instead of ASTM Type I portland cement.

At the lower superplasticizer dosage (2%), the difference in strengths of SMP and SNP concretes is negligible, whereas at the higher dosage (4%) the SMP concretes perform better than the SNP ones. This could be ascribed to the higher difference in the air contents of SMP and SNP concretes at the higher superplasticizer dosage (Table 6).

#### CONCLUSIONS

The following conclusions can be drawn:

1. The combined addition of fly ash and superplasticizer makes concrete as strong as that containing silica fume and superplasticizer, provided that ASTM Type III portland cement is used; this is particularly evident in concretes with relatively high cement factor (300 to 400 kg/m<sup>3</sup>), whereas in leaner cement mixes (255 kg/m<sup>3</sup>), silica fume performs a little better than fly ash.
2. By using ASTM Type I portland cement, strength of silica fume concrete is higher than that of fly ash concrete, the difference being higher for lean mixes (255 kg/m<sup>3</sup> cement).
3. By increasing the SMP superplasticizer dosage from 2 to 4%, concrete compressive strength is always increased in the presence of silica fume or fly ash independently of the cement type.

4. By increasing the SNP superplasticizer dosage over 2%, compressive strength is always increased, but not in the presence of both fly ash and ASTM Type I portland cement.

From the above results it appears that the SNP polymer is in general more effective as water reducer than the SMP one. However SNP seems to cause a certain retardation in cement hydration so that SMP concrete is in general stronger than SNP concrete when a very high superplasticizer dosage (4%) is used. Such a retardation effect appears to be significantly reduced when silica fumes and/or Type III portland cements are used, or when relatively high cement factors are adopted. Moreover, at higher superplasticizer dosages the air content in the SNP concrete mixes becomes higher than that of the SMP ones and this should furtherly increase the strength of SMP concrete with respect to that of the SNP when 4% superplasticizer dosage is used.

Superplasticized fly ash concrete becomes as strong as superplasticized silica fume concrete when Type III portland cement is used. Due to the higher C<sub>3</sub>S content and higher fineness, the hydration of this cement, produces a larger amount of Ca(OH)<sub>2</sub>. Therefore more calcium hydroxide is available for the pozzolanic reaction with fly ash or silica fume to form C-S-H which increases strength. The higher amount of available Ca(OH)<sub>2</sub> produced by hydration of Type III portland cement should favour more fly ash than silica fume because fly ash is potentially less reactive for the lower fineness and lower content of amorphous silica. Similarly, even if to a lower extent, an increase of the cement factor should favour more fly ash than silica fume.

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TABLE 1--ACTUAL COMPOSITION OF CONCRETES WITH A NOMINAL CEMENT FACTOR OF 255 kg/m<sup>3</sup> (ASTM PORTLAND TYPE I)

Mix No.	Type I cement factor (kg/m <sup>3</sup> )	Fly ash (kg/m <sup>3</sup> )	Silica fume (kg/m <sup>3</sup> )	Type and dosage of superplasticizer	W/C	W/B (*)	Slump (mm)
1	251	45	-	SNP - 2%	0.69	0.59	220
2	251	45	-	SNP - 4%	0.59	0.50	225
3	259	46	-	SMP - 2%	0.68	0.58	200
4	264	47	-	SMP - 4%	0.61	0.52	230
5	257	-	46	SNP - 2%	0.76	0.65	220
6	259	-	46	SNP - 4%	0.51	0.43	225
7	254	-	44	SMP - 2%	0.79	0.67	220
8	264	-	47	SMP - 4%	0.51	0.44	230

(\*) B= Binder: cement + fly ash or silica fume.

TABLE 2--ACTUAL COMPOSITION OF CONCRETES WITH A NOMINAL CEMENT FACTOR OF 300 kg/m<sup>3</sup> (ASTM PORTLAND TYPE I)

Mix No.	Type I cement factor (kg/m <sup>3</sup> )	Fly ash (kg/m <sup>3</sup> )	Silica fume (kg/m <sup>3</sup> )	Type and dosage of superplasticizer	W/C	W/B (*)	Slump (mm)	Air content (% by volume)
9	291	43	-	SNP - 2%	0.57	0.49	220	2.4
10	290	44	-	SNP - 4%	0.49	0.43	230	4.6
11	300	45	-	SMP - 2%	0.57	0.49	220	1.9
12	305	46	-	SMP - 4%	0.52	0.45	230	2.3
13	292	-	44	SNP - 2%	0.61	0.53	220	2.2
14	296	-	44	SNP - 4%	0.43	0.38	220	4.5
15	297	-	44	SMP - 2%	0.66	0.57	220	2.0
16	308	-	46	SMP - 4%	0.43	0.38	230	2.4

(\*) B= Binder: cement + fly ash or silica fume.



TABLE 3--ACTUAL COMPOSITION OF CONCRETES WITH A NOMINAL CEMENT FACTOR OF 340 kg/m<sup>3</sup> (ASTM PORTLAND TYPE I)

Mix No.	Type I cement factor (kg/m <sup>3</sup> )	Fly ash (kg/m <sup>3</sup> )	Silica fume (kg/m <sup>3</sup> )	Type and dosage of superplasticizer	W/C	W/B (*)	Slump (mm)
17	321	57	-	SNP - 2%	0.51	0.43	225
18	331	59	-	SNP - 4%	0.44	0.37	230
19	333	58	-	SMP - 2%	0.53	0.46	230
20	335	59	-	SMP - 4%	0.44	0.37	230
21	332	-	59	SNP - 2%	0.50	0.42	220
22	336	-	59	SNP - 4%	0.35	0.30	220
23	330	-	58	SMP - 2%	0.51	0.43	220
24	339	-	60	SMP - 4%	0.35	0.30	225

(\*) B= Binder: cement + fly ash or silica fume.

TABLE 4--ACTUAL COMPOSITION OF CONCRETES WITH A NOMINAL CEMENT FACTOR OF 400 kg/m<sup>3</sup> (ASTM PORTLAND TYPE I)

Mix No.	Type I cement factor (kg/m <sup>3</sup> )	Fly ash (kg/m <sup>3</sup> )	Silica fume (kg/m <sup>3</sup> )	Type and dosage of superplasticizer	W/C	W/B (*)	Slump (mm)
25	393	59	-	NSP - 2%	0.39	0.34	220
26	404	61	-	NSP - 4%	0.34	0.30	230
27	409	62	-	MSP - 2%	0.39	0.34	230
28	411	62	-	MSP - 4%	0.36	0.31	230
29	402	-	60	NSP - 2%	0.38	0.33	220
30	408	-	61	NSP - 4%	0.29	0.25	235
31	405	-	61	MSP - 2%	0.39	0.34	220
32	416	-	62	MSP - 4%	0.29	0.25	220

(\*) B= Binder: cement + fly ash or silica fume.

TABLE 7--ACTUAL COMPOSITION OF CONCRETES WITH A NOMINAL CEMENT FACTOR OF 340 kg/m<sup>3</sup> (ASTM PORTLAND TYPE III)

Mix No.	Type III cement factor (kg/m <sup>3</sup> )	Fly ash (kg/m <sup>3</sup> )	Silica fume (kg/m <sup>3</sup> )	Type and dosage of superplasticizer	W/C	W/B (*)	Slump (mm)
49	330	58	-	SNP - 2%	0.54	0.46	220
50	338	60	-	SNP - 4%	0.36	0.31	220
51	329	59	-	SMP - 2%	0.55	0.47	220
52	342	60	-	SMP - 4%	0.36	0.31	225
53	332	-	59	SNP - 2%	0.50	0.42	220
54	346	-	61	SNP - 4%	0.34	0.29	220
55	333	-	59	SMP - 2%	0.56	0.47	220
56	345	-	61	SMP - 4%	0.36	0.30	225

(\*) B= Binder: cement + fly ash or silica fume.

TABLE 8--ACTUAL COMPOSITION OF CONCRETES WITH A NOMINAL CEMENT FACTOR OF 400 kg/m<sup>3</sup> (ASTM PORTLAND TYPE III)

Mix No.	Type III cement factor (kg/m <sup>3</sup> )	Fly ash (kg/m <sup>3</sup> )	Silica fume (kg/m <sup>3</sup> )	Type and dosage of superplasticizer	W/C	W/B (*)	Slump (mm)
57	398	60	-	NSP - 2%	0.44	0.38	220
58	407	61	-	NSP - 4%	0.31	0.27	220
59	401	60	-	MSP - 2%	0.46	0.40	220
60	415	62	-	MSP - 4%	0.31	0.27	220
61	391	-	58	NSP - 2%	0.43	0.37	220
62	406	-	61	NSP - 4%	0.32	0.28	230
63	398	-	60	MSP - 2%	0.44	0.38	220
64	414	-	62	MSP - 4%	0.32	0.28	230

(\*) B= Binder: cement + fly ash or silica fume.

TABLE 5--ACTUAL COMPOSITION OF CONCRETES WITH A NOMINAL CEMENT FACTOR OF 255 kg/m<sup>3</sup> (ASTM PORTLAND TYPE III)

Mix No.	Type III cement factor (kg/m <sup>3</sup> )	Fly ash (kg/m <sup>3</sup> )	Silica fume (kg/m <sup>3</sup> )	Type and dosage of superplasticizer	W/C	W/B (*)	Slump (mm)
33	259	45	-	NSP - 2%	0.69	0.59	220
34	262	46	-	NSP - 4%	0.47	0.40	225
35	256	45	-	MSP - 2%	0.78	0.67	220
36	272	48	-	MSP - 4%	0.50	0.43	230
37	259	-	46	NSP - 2%	0.67	0.57	220
38	266	-	47	NSP - 4%	0.44	0.37	225
39	257	-	46	MSP - 2%	0.73	0.62	220
40	268	-	48	MSP - 4%	0.45	0.38	230

(\*) B= Binder: cement + fly ash or silica fume.

TABLE 6--ACTUAL COMPOSITION OF CONCRETES WITH A NOMINAL CEMENT FACTOR OF 300 kg/m<sup>3</sup> (ASTM PORTLAND TYPE III)

Mix No.	Type III cement factor (kg/m <sup>3</sup> )	Fly ash (kg/m <sup>3</sup> )	Silica fume (kg/m <sup>3</sup> )	Type and dosage of superplasticizer	W/C	W/B (*)	Slump (mm)	Air content (% by volume)
41	302	46	-	NSP - 2%	0.57	0.50	220	2.5
42	309	46	-	NSP - 4%	0.40	0.35	225	4.2
43	301	45	-	MSP - 2%	0.62	0.54	220	1.8
44	315	48	-	MSP - 4%	0.40	0.35	230	2.4
45	294	-	44	NSP - 2%	0.55	0.47	220	2.4
46	303	-	46	NSP - 4%	0.39	0.34	230	4.0
47	299	-	44	MSP - 2%	0.59	0.51	220	2.0
48	315	-	48	MSP - 4%	0.39	0.34	230	2.2

(\*) B= Binder: cement + fly ash or silica fume.

TABLE 9--CHARACTERISTICS OF SILICA FUME,  
FLY ASH, AND PORTLAND CEMENTS USED

	Silica fume	ASTM class F fly ash	ASTM Type I portland cement	ASTM Type III portland cement
SiO <sub>2</sub>	92.9	43.4	21.1	20.0
CaO	0.1	8.1	59.9	62.4
Al <sub>2</sub> O <sub>3</sub>	2.3	33.8	4.3	4.1
Fe <sub>2</sub> O <sub>3</sub>	0.1	4.7	3.3	1.9
MgO	1.4	2.4	2.6	2.2
K <sub>2</sub> O	0.2	0.0	0.5	0.6
Na <sub>2</sub> O	0.6	0.1	0.3	0.1
SO <sub>3</sub>	0.0	0.3	3.3	3.1
l.o.i.	2.0	6.9	4.2	4.9
C <sub>3</sub> S	-	-	51.8	61.0
C <sub>2</sub> S	-	-	14.7	9.4
C <sub>3</sub> A	-	-	5.7	9.4
C <sub>4</sub> AF	-	-	10.1	5.8
BET specific surface area (m <sup>2</sup> /g)	20.02	0.61	-	-
Blaine specific surface area (m <sup>2</sup> /g)	-	-	0.34	0.47
Setting time initial/final (hr:min)*	-	-	2:30/4:40	1:15/3:05
Compressive strength (MPa) on standard mortar mix ** at: 1 day	-	-	11.4	20.1
3 days	-	-	18.2	31.7
7 days	-	-	34.6	43.7
28 days	-	-	44.0	56.3

\* on cement paste.

\*\* w/c= 0.5; s/c= 3; specimen: 40x40x40 mm.

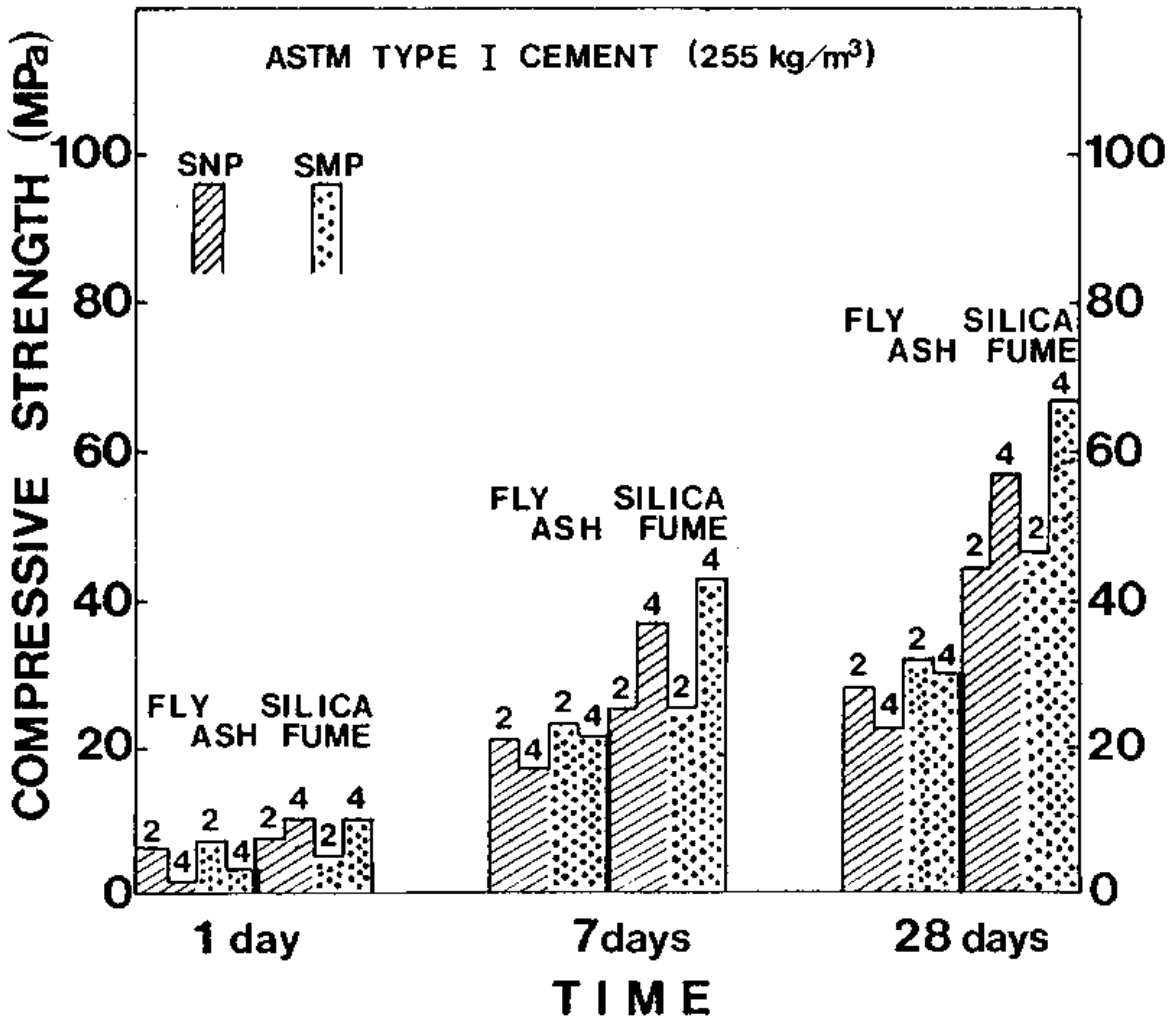


Fig. 1--Compressive strength of concretes with fly ash or silica fume (45 kg/m<sup>3</sup>); slump = 220 mm; ASTM cement Type I; cement factor = 255 kg/m<sup>3</sup>; figures on histograms indicate the percentage of superplasticizer by weight of cement; superplasticizer: SNP (sulphonated naphtalene polymer) or SMP (sulphonated melamine polymer)

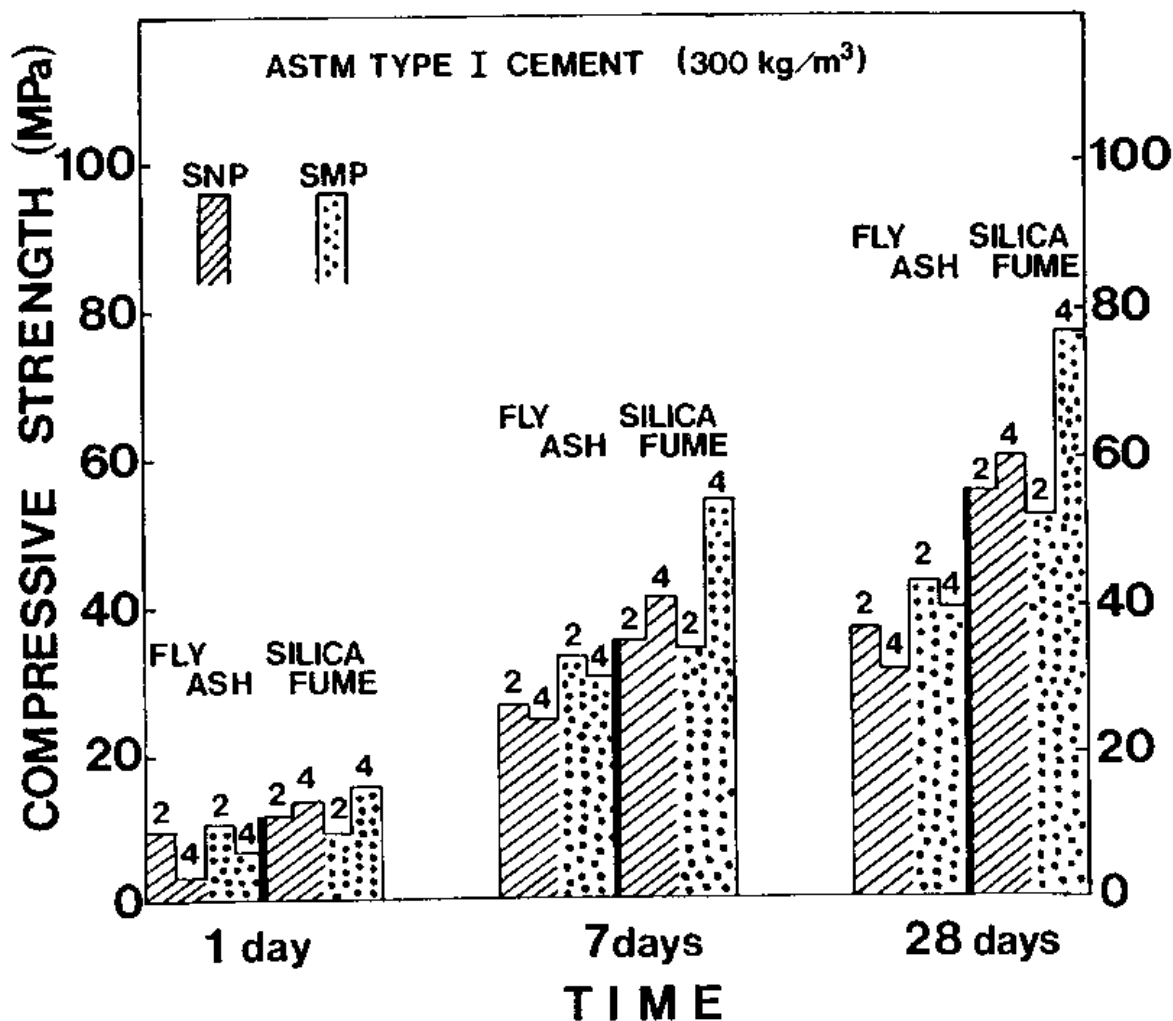


Fig. 2--Compressive strength of concretes with fly ash or silica fume (45 kg/m<sup>3</sup>); slump = 220 mm; ASTM cement Type I; cement factor = 300 kg/m<sup>3</sup>; figures on histograms indicate the percentage of superplasticizer by weight of cement; superplasticizer: SNP (sulphonated naphthalene polymer) or SMP (sulphonated melamine polymer)

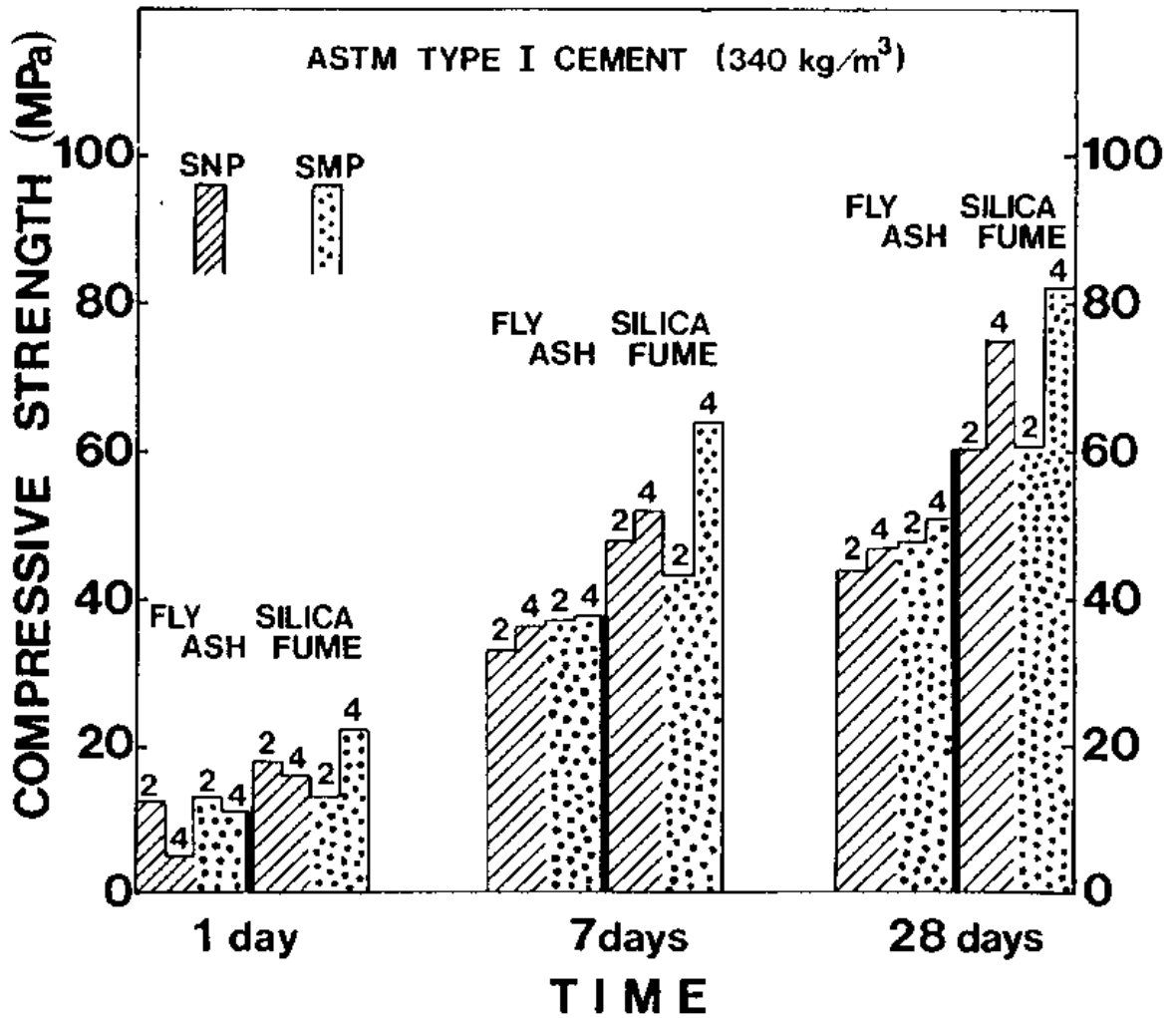


Fig. 3--Compressive strength of concretes with fly ash or silica fume (60 kg/m<sup>3</sup>); slump = 220 mm; ASTM cement Type I; cement factor = 340 kg/m<sup>3</sup>; figures on histograms indicate the percentage of superplasticizer by weight of cement; superplasticizer: SNP (sulphonated naphtalene polymer) or SMP (sulphonated melamine polymer)

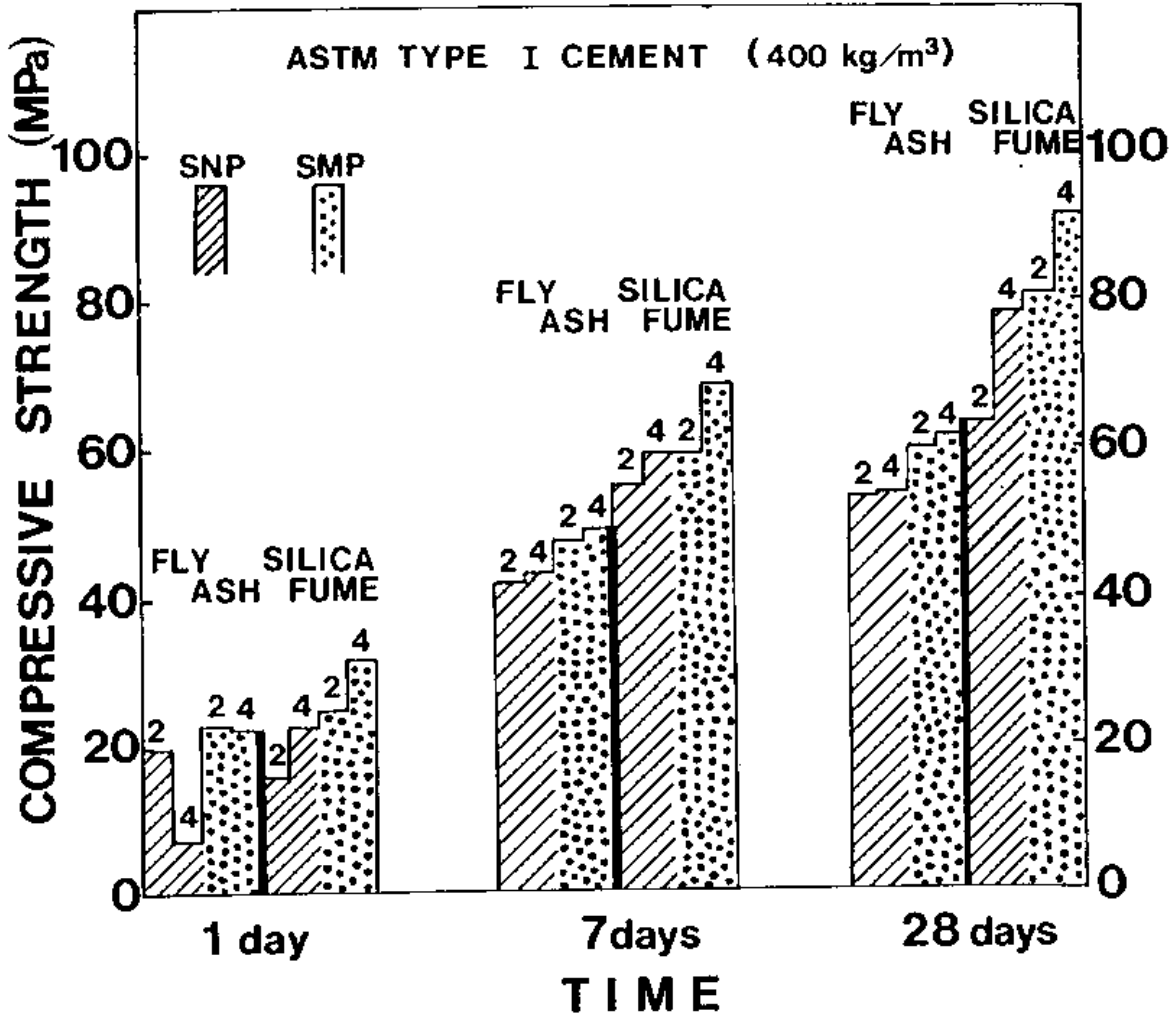


Fig. 4--Compressive strength of concretes with fly ash or silica fume (60 kg/m<sup>3</sup>); slump = 220 mm; ASTM cement Type I; cement factor = 400 kg/m<sup>3</sup>; figures on histograms indicate the percentage of superplasticizer by weight of cement; superplasticizer: SNP (sulphonated naphtalene polymer) or SMP (sulphonated melamine polymer)



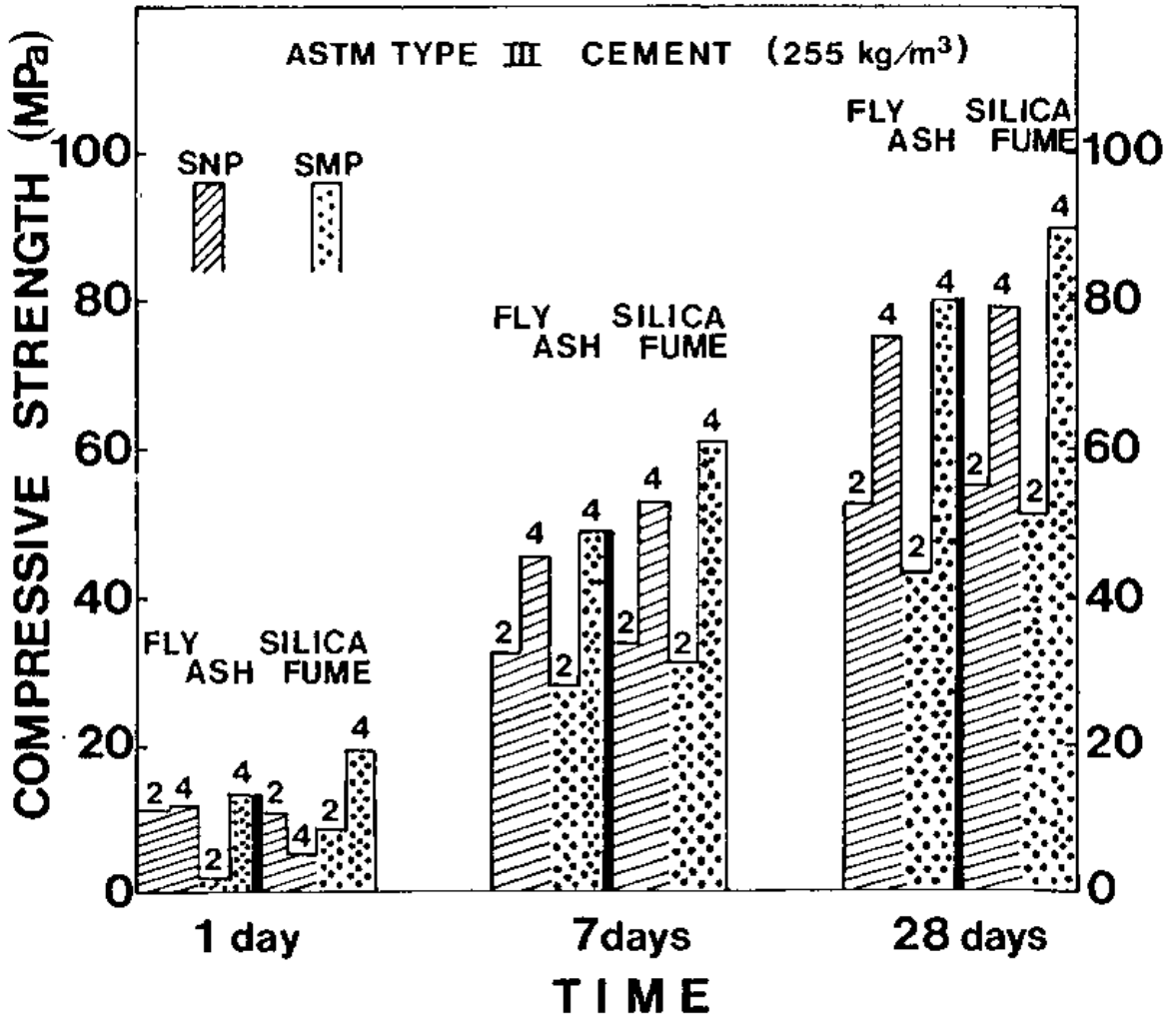


Fig. 5--Compressive strength of concretes with fly ash or silica fume (45 kg/m<sup>3</sup>); slump = 220 mm; ASTM cement Type III; cement factor = 255 kg/m<sup>3</sup>; figures on histograms indicate the percentage of superplasticizer by weight of cement; superplasticizer: SNP (sulphonated naphthalene polymer) or SMP (sulphonated melamine polymer)

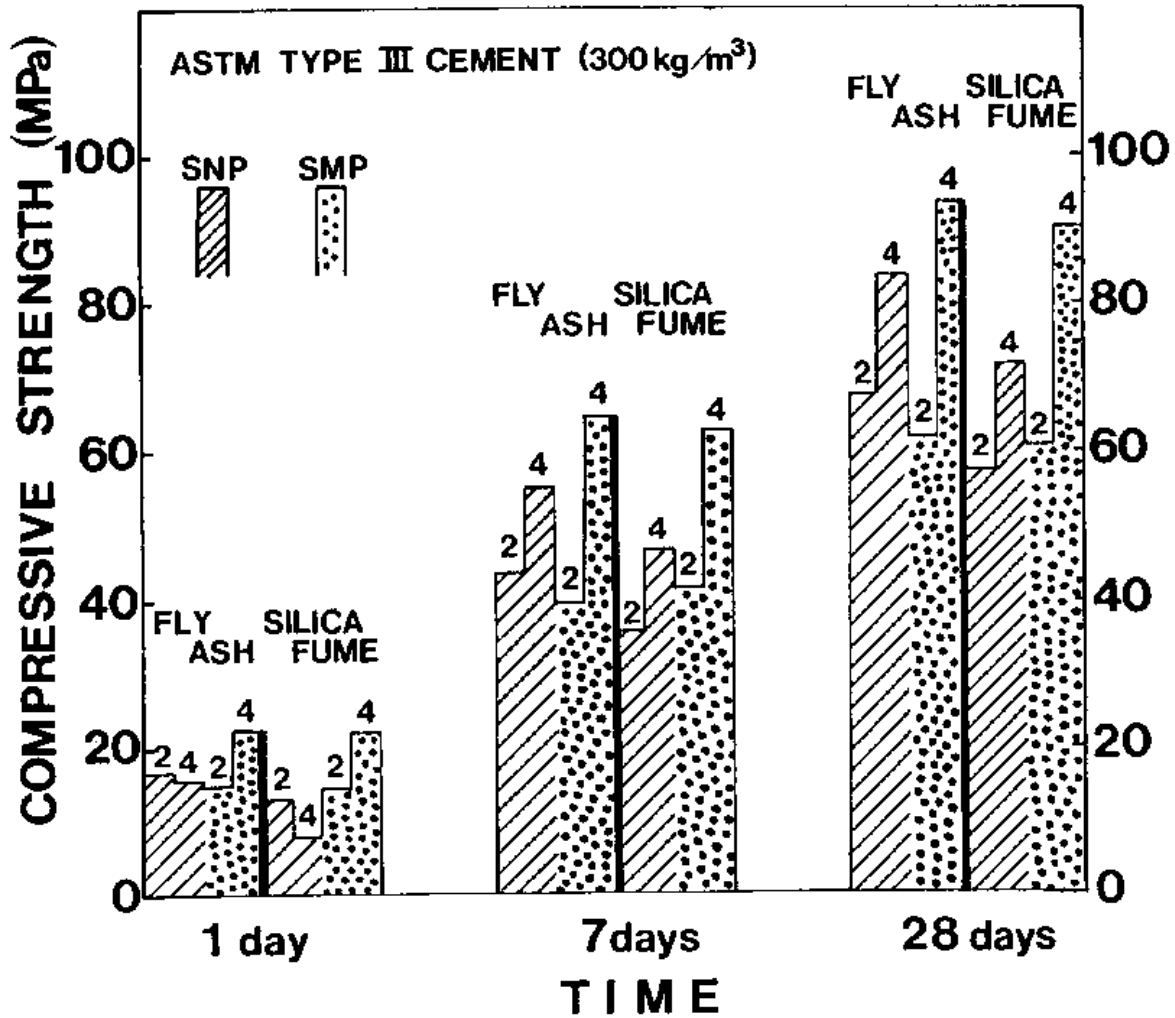


Fig. 6--Compressive strength of concretes with fly ash or silica fume (45 kg/m<sup>3</sup>); slump = 220 mm; ASTM cement Type III; cement factor = 300 kg/m<sup>3</sup>; figures on histograms indicate the percentage of superplasticizer by weight of cement; superplasticizer: SNP (sulphonated naphtalene polymer) or SMP (sulphonated melamine polymer)

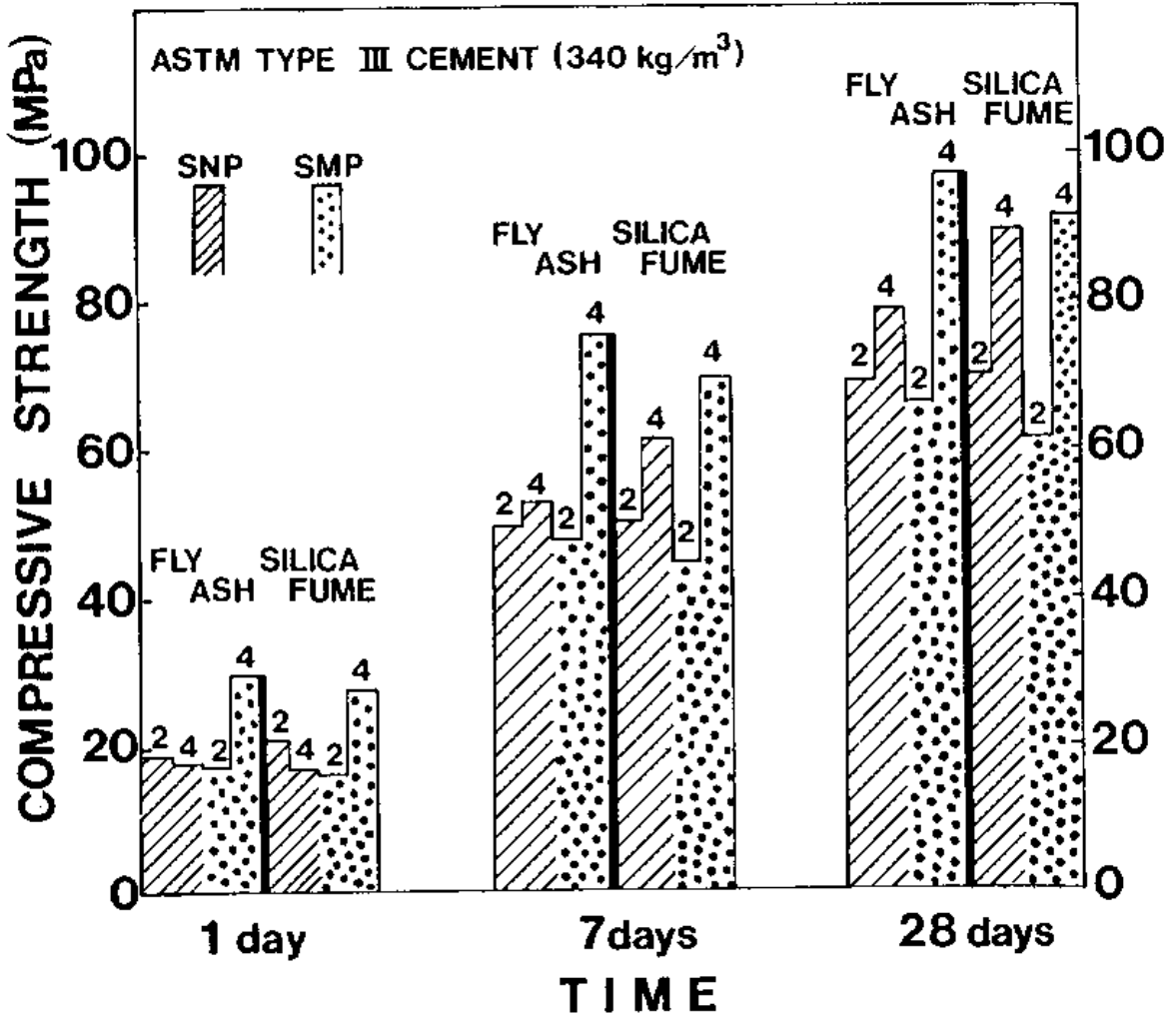


Fig. 7--Compressive strength of concretes with fly ash or silica fume ( $60 \text{ kg/m}^3$ ); slump = 220 mm; ASTM cement Type III; cement factor =  $340 \text{ kg/m}^3$ ; figures on histograms indicate the percentage of superplasticizer by weight of cement; superplasticizer: SNP (sulphonated naphthalene polymer) or SMP (sulphonated melamine polymer)

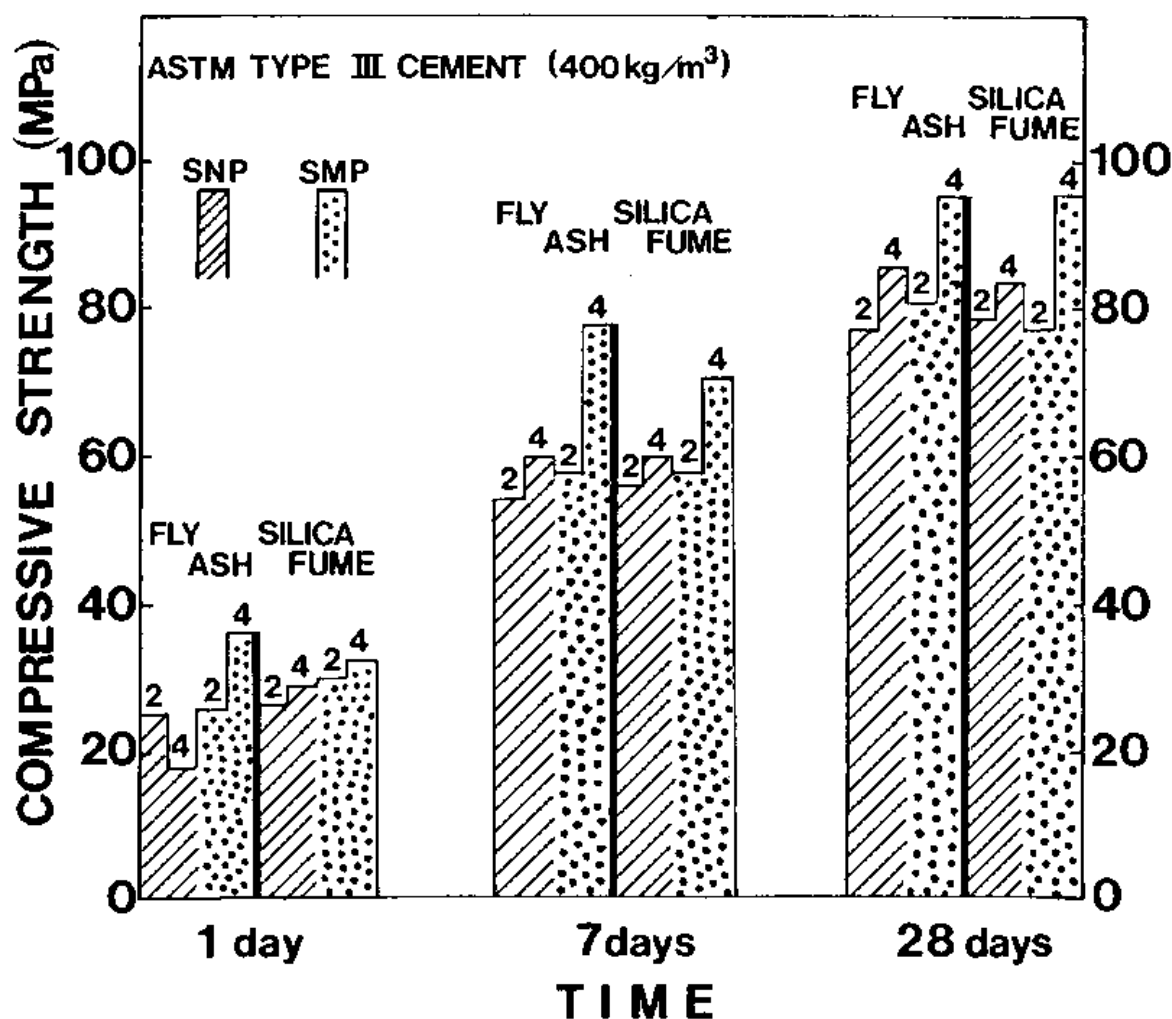


Fig. 8--Compressive strength of concretes with fly ash or silica fume ( $60 \text{ kg/m}^3$ ); slump = 220 mm; ASTM cement Type III; cement factor =  $400 \text{ kg/m}^3$ ; figures on histograms indicate the percentage of superplasticizer by weight of cement; superplasticizer: SNP (sulphonated naphthalene polymer) or SMP (sulphonated melamine polymer)