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ULTRAFINE PARTICLES FOR THE MAKING OF VERY HIGH STRENGTH CONCRETES

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ABSTRACT

The manufacture of very high strength concrete (28-day compressive strength higher than 80 MPa) often involves the addition of ultrafine particles together with large proportions of organic admixtures. This article compares the effectiveness of different fillers and their mixture. Silica fumes are found to be the most effective addition, and they are looked into more particularly in terms of their effect on the properties of mortars according to their proportion (optimum proportion) and quality (chemical composition).

Introduction

The production of concretes which are workable when fresh and have a 28-day compressive strength higher than 80 MPa is currently possible owing to superplasticiser admixtures which make leading to very low water-cement ratios (less than 0.30). The use of ultrafine particles, i.e. grain size smaller than that of cement, facilitates this production, as a result of their action:

i) on the physical level (filler effect, when the grains fill the voids between those of cement, reducing the water requirement)

ii) on the chemical level (for siliceous particles, a pozzolanic effect, reaction of silica with lime released by the cement). Depending on available products and desired concrete properties, it is important to establish quantitative and qualitative selection criteria in order to obtain the required material at the best cost.

It is consequently important to compare the performance of different compositions of binding pastes, which are designed to give the concrete a certain workability and a given strength, two properties which are generally contradictory. One objective way for establishing a classification is to compare at a given time compressive strengths of mortars in which **the volume and fluidity of different tested pastes have been kept constant** (fluidity being determined by a test similar to the Marsch Cone Test - see figure 1).

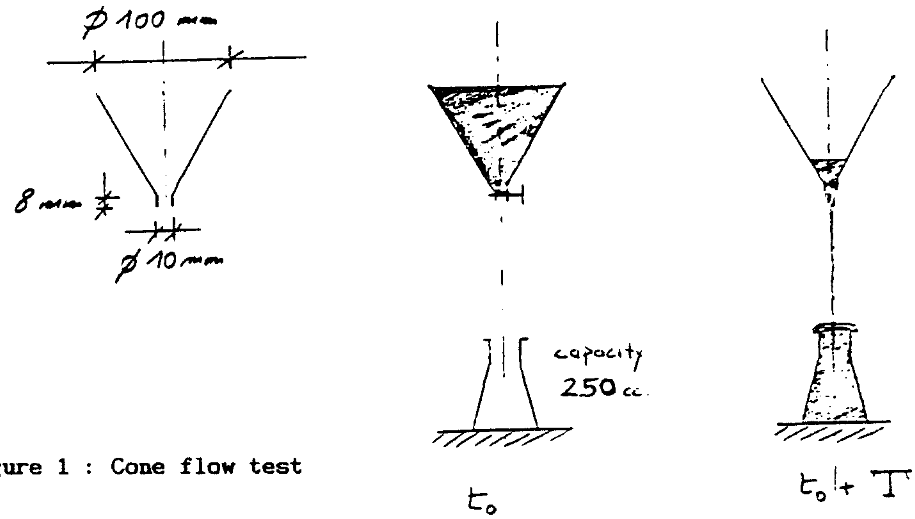


Figure 1 : Cone flow test

Rheological properties also depend on the amount of fluidizing admixture used. To the extent that one wishes to characterize the "mineral part" of the paste and not the organic admixture, grains are saturated with a superplasticiser so as to get the lesser water demand (see figure 2). The choice of relative proportions of different binders then leads to a superplasticiser proportion (increasing with the specific area). The water proportion corresponds to a given flow time (5 seconds in our tests). Mechanical strengths thus obtained with mortar reflect the capacity of the cement/ultrafine mix to give the grain mixture its high strength.

This paper examines, first of all, the different types of ultrafine particle and their mixture. Then, the case of silica fumes is studied in greater detail, considering the amounts to be used and their performance in relation to their chemical composition.

Linear model of grain mixture packing density

A mathematical model has already been presented (1,2) designed to predict the packing density of a grain mixture based upon its particle size distribution and **specific packing density values** (packing density of each monodimensional section piled separately) using the same methods applied to the overal mixture. We applied the model to the mix design of plasticised cementitious pastes, and we showed that the following expressions gave a theoretical packing density increasing with the real packing density of the different mixtures :

$$c = \inf_{t>0} \frac{\alpha(t)}{1 - \int_0^t f(t,x)y(x)dx - [1 - \alpha(t)] \int_t^{+\infty} g(t,x)y(x)dx}$$

* c is the theoretical packing density of the mixture described by its particle size distribution y (with unit integral)

* $\alpha(t) = 0.39 + 0.022 \ln t$

(α is the specific packing density of the particles of diameter t, expressed in μ m)

* $f(t,x) = f(z=t/x) = (1-z)^{3.1} + 3.1\, z\, (1-z)^{2.9}$

* $g(t,x) = g(z=x/t) = (1-z)^{1.6}$

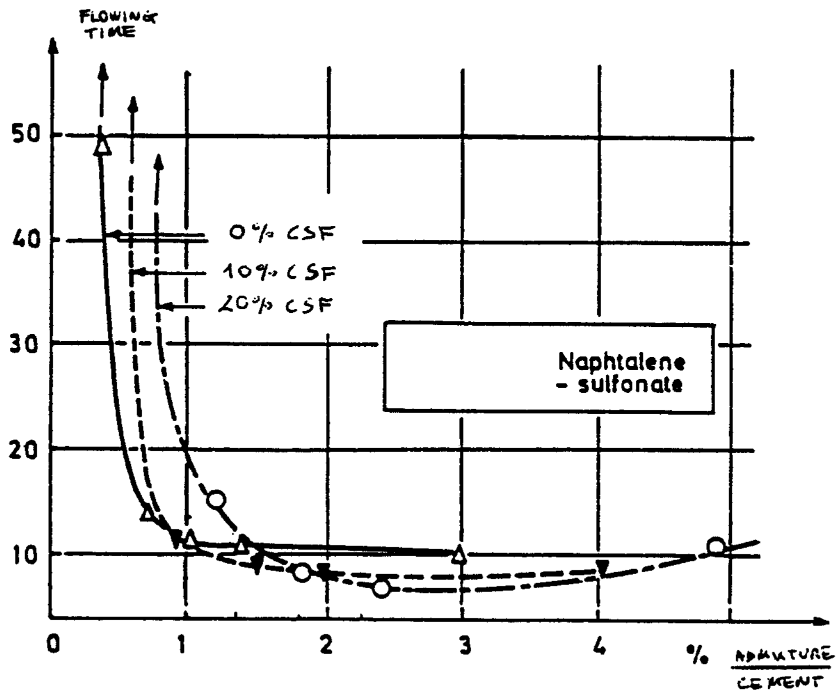
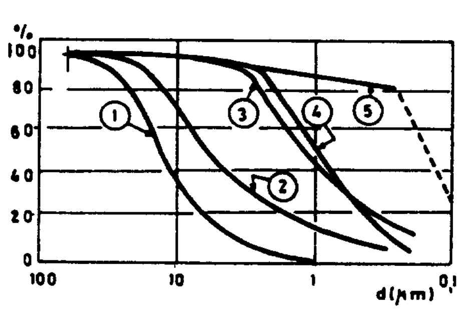


Figure 2 : Cone flow time of different pastes as a function of admixture proportion (CSF: Condensed Silica Fume)



1) Portland cement
2) Limestone filler
3) Limestone ultrafine filler
4) Siliceous ultrafine filler
5) Silica fume

Figure 3 : Particle size distribution of different binders [1,2]

The particle size distributions of different cementitious materials were measured with the sedigraph (see figure 3). The application of the model then gives the ternary diagrams shown in figure 4, representing the locations of iso-packing density points. It is thus possible to select various cement-ultrafine mixtures of interest in different respects.

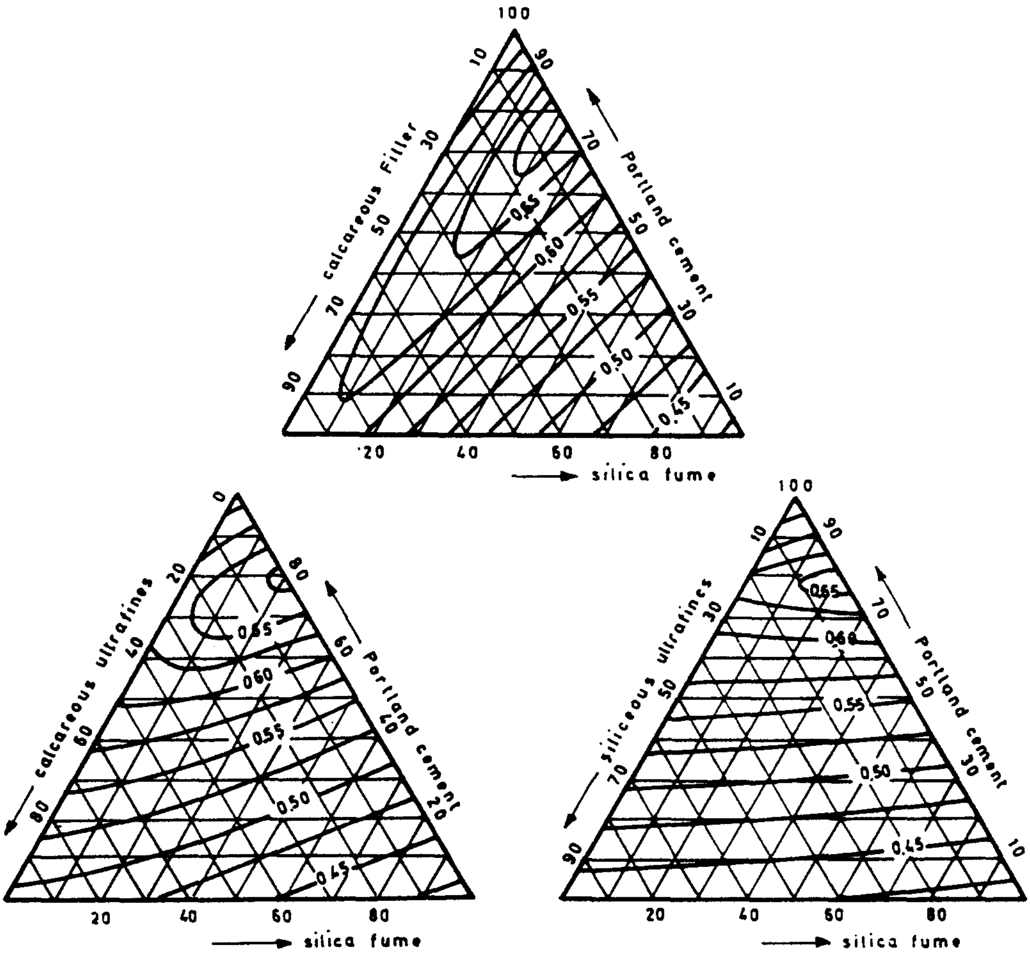


Figure 4 : Ternary diagrams predicted by the linear model of grain mixture packing density [1,2]

Hierarchy between types of ultrafine particles

The mineral binders tested were the following :

- ordinary portland cement (with a strength of 55 MPa at 28 days) with a high-silica content, chosen for its very good compatibility with superplasticisers, whose composition according to Bogue was as follows :
  C_3S = 63.30 %, C_2S = 17.72 %, C_3A = 1.62%, C_4AF = 8.47 %, Gypsum = 4.06%, $CaCO_3$ = 2.59 %, CaO = 0.5 %.
- Limestone filler, with grain size between cement and ultrafine particles
- Limestone ultrafine filler(average size 1 μm)

- Siliceous ultrafine filler from grinding (average size 1 μm),
- Two silica fumes.

All those mixes have been prepared with naphthalene sulfonate formaldehyde.

Using these products, 12 mortars were prepared having the compositions and strengths shown in table 1; mortar No. 1 served as a control.

Table 1 : Composition and mechanical strength of mortars (I series)

N°	Rilem Sand g	OPC g	Fillers and ultrafine particles g		Admixtures g	Water g	w/c	Flowing time LCL s [13]	Flexural Stength MPa	Compressive Strength MPa
1	1350	529	-	-	7,9	148	0,280	16 s	9,5	74
2	"	520	Silica Fume N°1 80	-	10,7	114	0,219	4 s	14,5	103
3	"	481	ultrafine calcareous 103	-	10,2	125	0,260	15 s	11,3	77
4	"	467	ultrafine siliceous filler 111	-	10,1	126	0,270	10 s	11,6	81
5	"	489	silica fume N°I 43	ultrafine calcareous 52	10,3	122	0,249	3 s	12,8	90
6	"	348	calcareous filler 149	silica fume N°1 40	9,8	132	0,379	2 s	9,9	72
7	"	553	industrial silica-fume 27	-	9,6	128	0,231	11 s	10,8	(94)
8	"	535	53	-	10,6	122	0,228	5 s	14,4	96
9	"	514	77	-	11,4	117	0,228	4 s	14,2	101
10	"	495	99	-	12,1	113	0,228	6 s	15,4	105
11	"	468	117	-	12,5	113	0,241	12 s	15,9	101
12	"	443	133	-	12,9	114	0,257	17 s	13,0	96

It is noted first of all that compressive and bending strengths show good correlation. In the area investigated, these properties consequently appear to be controlled essentially by the **packing density of the binding phase**. This is also the case for concrete, until one reaches a limit due to the specific strength of the aggregate, for compressive strengths of about 110/120 MPa.

Mortars Nr 2-3-4 have, within the limits set in the introduction, quite the optimum compositions for cement/ultrafine particles binary mixes, respectively for silica fume, calcareous filler and siliceous filler. The very high fineness of silica fume, combined with its pozzolanic activity, places it far ahead of grinding mill products. For the latter, siliceous filler show a certain chemical activity in spite of their initially crystalline nature, giving them a superiority over limestone, in spite of lower efficiency regarding the filler effect. The activity of calcareous products in this type of mortar has however been demonstrated by Buil et al. [3]. However, in the present case, it was not observable owing to the very low aluminate content of the cement.

In compositions Nr 5 and Nr 6, an attempt was made to determine the value of associating less noble products with silica fume. Hence, the price of silica fume is supposed to increase in next years. Further, it may be reasonable to limit the amount of silica fume to about 10 to 15% achieving in the long term the maintenance of a sufficiently alkaline pH. The comparison of compositions Nr 5 and Nr 8 then shows that the composition with 10 % silica fume (Nr 8) offers higher performance than the mix containing 10 % limestone, 10 % silica fume and 80 % cement (Nr 5), although slightly lower in water. Formula Nr 6 shows - by comparison with the control - that it is possible to reduce the cement content of a high-strength concrete by about 34 % without modifying its strength, by substituting a quasi-inert fine for the cement, and adding a small amount of silica fume. This type of material certainly offers a lower hydration heat, as well as more stable workability, important properties for the production of large components and for placement on the site respectively.

Further investigations on silica fumes

Optimum proportion

We first looked into the problem of the optimum amount of silica fume addition used in concretes to obtain maximum mechanical strength. Using additions in a mortar, with the adjustment of the admixture content, Buil et al. [4] found values between 40 and 50 % for the ratio between silica fume weight. Seki et al. [5] using the same approach, but on concrete, obtained a value of 26 % . However, **applying a constant paste content and constant fluidity, the increase in strength obtained indeed translates the original contribution of silica fume**. This improvement would not have been achievable by the addition of cement, which would have necessarily reduced workability with a constant paste content, or increased the past volume for the same workability.

Formulas Nr 1-7-8-9-10-11-12 show the variation in the water/cement ratio and compressive and bending strengths with the proportion of silica fume. Surprisingly, the cement content increases for a small proportion of ultrafine particles: this is the **"roller bearing" effect** which we described earlier [6]. Things occur as if a highly diluted suspension of silica fume in water was more fluid than pure water ! A similar result was also found by Yogendran et al. [7], who observed that a substitution of 5 % silica fume for a concrete whose admixture proportion is kept constant does not cause an increase in water requirements. In fact, a small addition of silica fume prevents the sedimentation of the cement and thus facilitates its flow. This is probably to be linked with the improvement in concrete pumpability, frequently observed with low silica fume proportions.

The water/cement ratio is surprisingly stable for silica fume contents ranging from 5 to 20 %. Within this range, the increase in strength is consequently essentially due to the pozzolanic activity of silica fume. It is known that this activity culminates at about 24 % [8], a level beyond which all the lime released by the cement is consumed. It is also as of this key level that the effectiveness of silica fume as a filler decreases (see figure 4). **The optimum silica fume content for obtaining high strength is consequently around 20 to 25 %** . It is in this proportion that ultrafine particles best fill the voids of the cement grains, with which they can then combine to form hydrates participating in the strength of the material. It is however noted that the mechanical gain is faster with smaller proportions. Considering the cost of silica fumes and of the admixtures, **the practical** (economic) **optimum is located rather towards 10 % silica fume in relation to cement weight** [1].

Silica fume selection criteria

It is known that silica fume is a by-product of the manufacture of silicon and of its alloys. Depending on the composition of the alloys, on the secondary products added to the main constituents, on the manufacturing method, and so on, silica fume properties can vary considerably.

For clarification, we carried out a series of tests on six silicas coming from different sources. While this does not constitute a sufficient statistic sampling, it does however make it possible to observe differences in behaviour in connection with physical and chemical properties. Silica No.1 is a special silica from the manufacture of zirconium. Its cost makes it ill-suited to civil engineering applications, but its effectiveness and its high purity make it a particularly interesting laboratory product.

To evaluate the utilization properties of these fumes, we attempted to :

- quantify the **"rheological" performance** levels ; for this, we measured the workability of mortars with a constant proportion ;
- estimate the **pozzolanic performance** levels by measuring the strengths reached by the same mortars.

We then attemped to relate these utilization properties by comparing them with chemical analyses and specific area measurements. The results of these investigations are given in table 3. The compositions of the mortars appear in table 2.

Table 2 : Mortar compositions (II series)

Mortars	RILEM Sand	Cement OPC	Silica Fume	Superplasti- -cizer	w/c	Flowing time "LCL" [13]
II Series	1350 g	544 g	100 g	12,2 g	0,25	depending on silica-fumes

An examination of Table 3 allows the following remarks:

i) from the viewpoint of the BET specific surface, **fineness has no direct effect either on rheological or pozzolanic properties.** It is hence the coarsest silica (No. 1) that gives the best performance. In fact, the grain size range of silica corresponding to the specific surface (about 0.1 µm for 20 m²/g of BET surface) is so fine that its granular interactions with cement are very weak (cement grains all being greater than a micro-meter). In our opinion, this effect is due to a more or less extensive aggregation of silica grains, an aggregation which can be seen on the grading curves of figure 5, measured with the sedigraph [9].

Table 3 : Characteristics and performances of six condensed silica-fumes

Silica Fumes		1	2	3	4	5	6
Specific Areas (B.E.T.)		14.2 m²/g	22,3 m²/g	21,6 m²/g	22,2 m²/g	22,2 m²/g	19,3 m²g
	SiO_2	91.50 %	97,35 %	88,75 %	92,83 %	96,50 %	93,30 %
	Al_2O_3	5,78 %	0,03 %	0,08 %	0,02 %	0.03 %	0,02 %
	Fe_2O_3	0,16 %	0,12 %	1,60 %	0,19 %	0,06 %	0,30 %
	MgO	0,03 %	0,19 %	1,48 %	0,54 %	0.24 %	0,38 %
Chemical compositions	CaO	0.08 %	0,10 %	0,66 %	0,16 %	0,01 %	0,12 %
	Na_2O	0,12 %	0,12 %	0,71 %	0,24 %	0.26 %	0.76 %
	K_2O	0,03 %	0,23 %	2,41 %	1,76 %	0,47 %	1,40 %
	ZrO_2	1,10 %	-	-	-	-	-
	alkalies	0.20 %	0.35 %	3,12 %	2,00 %	0,73 %	2,16 %
	carbon	-	1,06 %	1,59 %	2,59 %	0.89 %	2,75 %
Mortars: (II series. flowing time L.C.L. workabilimeter		2"	5"	7,5"	10,5"	5"	9,5"
Compressive Strength at 28 d.		113 MPa	101 MPa	87 MPa	95 MPa	94 MPa	92 MPa

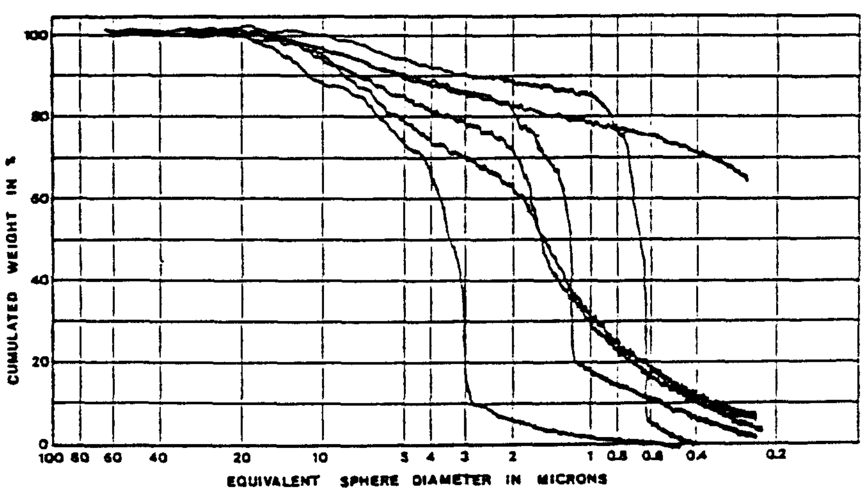


Fig. 5: Grading curves of different silica fumes (Sedigraph measurement)

These measurements show the particularly **high degree of agglomeration** of a silica fume in suspension in a physical and chemical environment representative of that of Very High-Strength concrete (pH 12.5, presence of calcium ions). The average size of the secondary grains was about one micrometer, or 100 times the average size of the basic grain ! Let us however point out that this curves should just be regarded as an illustration of the "particle-size instability" of silica fume in a cement paste. It is in fact probable that sand and cement grains act as grinding agents during the mixing of the VHS concrete, so that the actual particle-size distribution of silica fume is shifted toward the small sizes in relation to the preceding figure. However, it is not excluded that silica fume is partially aggregated during its formation. This would indicate a "sintering" phenomenon whose extent depends on the chemical and thermal conditions prevailing during cooling.

ii) **The purity of silica fume**, i.e. the percentage of SiO_2, **is not at first sight a decisive criterion** because, here too, it is the sample of the lowest purity (Nr 1) which gives the best strengths and the best workability. However, setting aside this sample Nr 1, the silicas investigated come from the manufacture of high silicon alloys. Certain authors (Regourd [10]) have examined silica fumes containing only 50 to 60 % SiO_2. Their pozzolanic properties were then clearly lower. Further, mechanical strength is less sensitive to marginal fluctuations in silica content when the ultrafine content approaches (as is the case) 20 % of the weight of the cement, practically exhausting all the avaiblable lime.

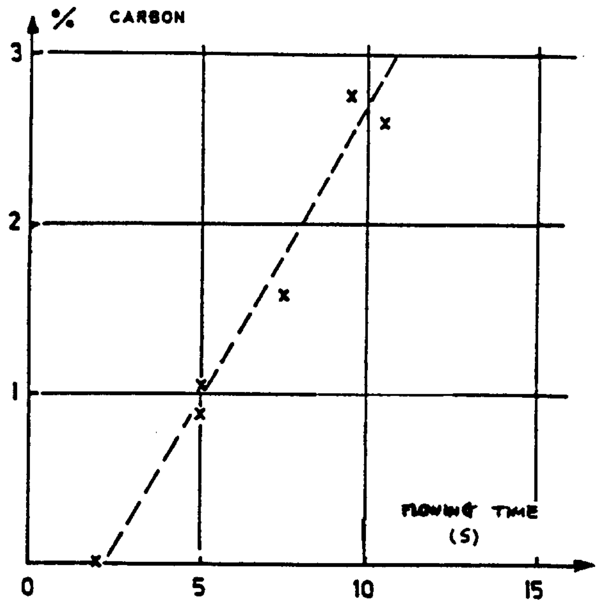


Figure 6 : Relationship between carbon content and workability

- **Carbon content**, corresponding to the more or less dark colour of silica fumes, **is related to a great extent** (in our samples) **to rheological performance levels** (see figure 6). It is known that this carbon comes from the combustion of organic matter (coal or wood chips) added to the constituents of silicon alloys. With the optical microscope, one observes wastes which are larger than the silica grains (of the order of 10 microns in size). These particles do not appear to exercise directly any harmful rheological effect, as was corroborated by the addition of carbon black to a mortar. Its presence indicates, rather, a history of temperatures, moreover responsible for the rheological quality of the by-product, perhaps as a result of grain aggregation.

Let us point out that a similar effect was reported by Osbaeck [11] for fly-ash. For this product (which, apart from its size, has many points in common with silica fume), a correlation is observed between water requirements and carbon content.

- The significant chemical parameter with respect to pozzolanic performance could be the alkali proportion (see figure 7). Based upon present knowledge regarding pozzolanic activity [12], one should expect an acceleration of the kinetics of silica attack with an increase in the proportion of alkalis. Alkalis however appear to reduce the strength of the material.

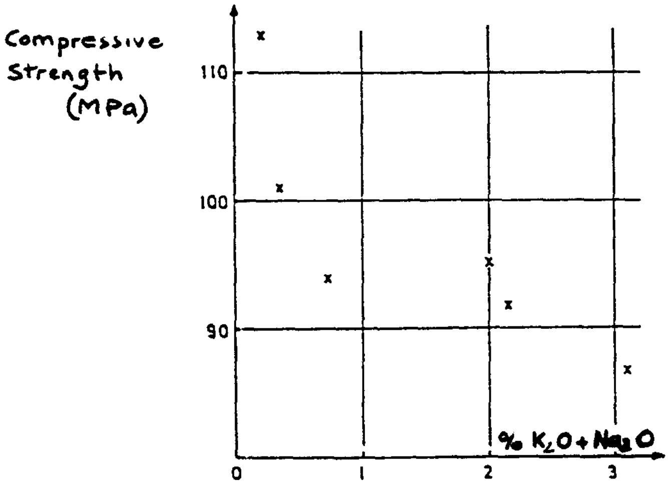


Figure 7 : Relationship between strength and alkali proportion

Table 4: Compositions of mortars (III series)

MORTAR "Co"

Sand RILEM	Cement OPC 55	Silica Nr 1	Superplasticizer	W/C
1350 g	544 g	100 g	12.2 g	0.25

MORTAR C_1 : C_0 + KOH (K^+/SiO_2 = 1 %)
C_2 : C_0 + KOH (K^+/SiO_2 = 2 %)
C_3 : C_0 + KOH (K^+/SiO_2 = 3 %)
C_4 : C_0 + KCl (K^+/SiO_2 = 1 %)
C_5 : C_0 + KCl (K^+/SiO_2 = 2 %)
C_6 : C_0 + KCl (K^+/SiO_2 = 3 %)

Figure 8 shows the compressive strength of mortars at 28 days, giving the mean values plus or minus the standard deviations of the different tests. A general decrease is in fact observed, the potash-chloride difference not being significant for the same proportion of alkalis, showing that what is involved is a direct effect of the potassium ion and not a consequence of the probable rising of the pH.

Conclusions

After having reviewed the conditions - which we consider to be necessary - for carrying out meaningful comparisons between mineral additives for the production of very high strength concretes, we can state the following conclusions :

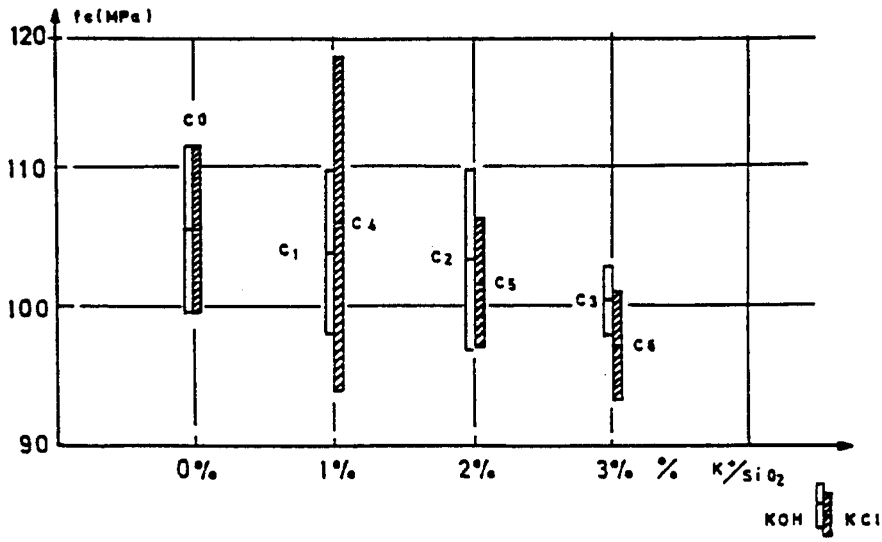


Figure 8: Evolution of strength with increasing addition of alkalis

a) compared with the use of a single OPC as a binder for a high strength concrete, the addition of grinding mill ultrafine particles (average size of the order of 1 micrometer) improves the strength of the material, probably with a slight superiority of siliceous products - a result to be confirmed however for cements containing aluminates.

b) silica fume constitutes a more effective product to be used pure if what is primarily expected is strength, and mixed with less active fillers when one wishes to reduce the proportion of cement.

c) the optimum silica fume proportion is between 20 and 25 % in weight of cement. However, a proportion of half that amount of the product is what will lead to an economical material, easy to place and of dependable durability.

d) the different industrial silicas available do not all have the same quality from the standpoint of their incorporation in concrete : they exhibit differences in workability and strength, these aspects not being interrelated.

e) the water requirements of material containing silica fume increases indirectly with its carbon content, which can be evaluated visually by the colour of the by-product.

f) binding properties of fumes sufficiently rich in silica (% SiO_2 > 85%) appear to depend primarily on the alkali content (Na_2O, K_2O), which must be as low as possible.

Additional tests are however necessary for the confirmation of these last results, and for deducing criteria enabling the classification of silica fumes into different grades.

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