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USE OF FLY ASH, SILICA FUME, SLAG AND NATURAL POZZOLANS IN EUROPE: FUTURE DIRECTIONS

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HISTORY OF THE ANCIENT USE OF POZZOLANIC MATERIALS IN EUROPE.

Fly ash, slag, silica fume and other siliceous materials, such as natural pozzolans, have been largely used in Europe.

The use of natural pozzolan-lime mortars and concrete was in use in Europe much before the invention of portland cement in the 19th century. The Romans made wide use of a volcanic material based on a zeolitic tuff discovered in Pozzuoli at the Bay of Naples and thus this material become popularly known all over the world as pozzolan or pozzolan. When other materials reacting with lime were found in other countries, such as Germany, France, Spain, the term of pozzolan was used to indicate any pozzolanic material, independently of its geological origin and chemical composition.

As the Romans learnt the art of construction developed by the Greeks, it is not surprising to know that natural pozzolan-lime concrete has been used in Greek constructions dating 700 B.C. (1).

According to Lea (2) the Romans have also used the first artificial pozzolan from crushed tiles recovered by old deteriorated constructions. Natural pozzolans based on trass, a vulcanic tuff, have been used in old Roman buildings along the Rhine in Germany (2). Trass deposit have also been discovered in Rumania and U.S.S.R. (1).

Many of the Roman building constructions, such as the Pantheon in Rome, or hydraulic structures, such as the famous Roman aqueducts, are in excellent condition even today in testimony of the long-term durability of cementitious products based on pozzolan.

2. PRESENT USE AND FUTURE DIRECTIONS OF POZZOLANIC MATERIALS IN EUROPE

European countries such as Germany, France, U.S.S.R., Italy, Greece and the Netherlands have had a long history of interest in saving energy and therefore since a long time they are engaged in the manufacture of large amounts of portland blended cements containing pozzolanic materials such as slag and natural pozzolans. Recently there is interest also in Europe, as it occurs in North America since a long time, in utilizing pozzolanic materials in the form of concrete ingredients rather than as components of blended cements; this is particularly true for by-products materials such as silica fume and fly ash.

2.1 Portland blended cements

Portland blended cements (3,4) are widely manufactured and used in Europe since the 19th century. Standard specifications exist in different European countries for pozzolan and slag cements. However, due to various reasons, in some countries only one of the two mentioned above blended cements is really produced on large scale. For instance in Italy, which is the biggest producer of cement in Western Europe more than 40% of the cement (36 million metric tons per year) is of portland-pozzolan type containing about 25% pozzolan, whereas slag cement is about 7% only. This difference in the amounts of pozzolan and slag cement could be ascribed to both the large availability of natural pozzolans all over Italy and the ancient tradition in the use of natural pozzolans. Similar reasons could explain why all portland cement manufactured in Greece generally contains 10% of volcanic pozzolan from Santonni Island, called Santonni earth (1).

On the other hand, the amount of pozzolan cements produced in Western Germany is very small. Not more than 50000 metric tons per year of natural pozzolan is used for manufacturing blended portland cements (1). Slag cement is much more popular than pozzolan cement in Western Germany, probably because this country is a very big producer of iron in Europe, so that the iron blast-furnace slag is available in very large amounts.

Since natural pozzolan and iron blast furnace slag are generally available in form of coarse particles these materials have been preferably used since the 19th century to make blended cementy by integrinding portland cement clinker, gypsum and pozzolan or slag in the cement mill. With the advent of fly ash, which is approximately as fine as portland cement, the grinding process of the pozzolan at the cement mill is not necessarily required and only a blending process at the separator is carried out. Due to the energy saving caused by this change in the process, fly ash is replacing natural pozzolan in many countries of Europe to manufacture portland-pozzolan cement. On the other hand, many European countries, which did not produce portland-pozzolan cement in the past time for lack of local natural pozzolan, are starting in manufacturing fly ash-portland cement.

2.2 Advantages of portland blended cements over portland cement

Besides the energy saving for the cement producer in manufacturing portland blended cements, there are some technical advantages for the users of pozzolan or slag cements. Table 1 summarizes the improvement in concrete performances with portland blended cements replacing portland cement.

Table 1 Technical improvements in concrete performances with pozzolan or slag cements replacing portland cement

EFFECT	CONCRETE STRUCTURE BENEFIT		
Reduction in heat development	Dams and other massive structures		
Increase in concrete sulfate resistance	Structures exposed to sulfate attack		
Reduction in chloride penetration (improved protection of embedded items against corrosion, i.e. rusting, oxidation, etc.)	Reinforced concrete for marine structures and structure exposed to deicing agents		
Reduction in alkali- aggregate reaction	Concrete with reactive aggregates		

Reduction in generation of heat development is substantially due to the lower content of portland cement. Figure 1 shows the heat developed by portland cement and the corresponding portland blended cements containing 25% of slag or natural pozzolan.

Improvement in the concrete sulfate resistance is mainly due to the reduction of the free time resulting from the hydration of the cement and thereby to the reduction in the amount of gypsum; Fig. 2 shows the change in length of concrete specimens exposed to a 10% Mg SO₄ aqueous solution: the use of slag cement and in particular of pozzolan cement instead of portland cement reduces the expansion caused by the sulfate attack.

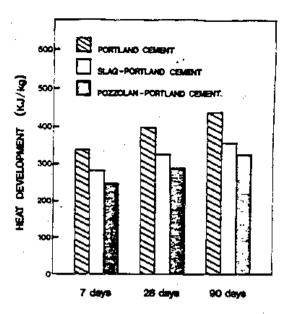


Fig. 1 Generation of heat hydration from portland cement and blended cements (25% of stag or fly ash type F).

Chloride penetration through concrete is source of danger since it promotes corrosion of reinforcement. Chloride penetration occurs in a good agreement with the Fick's law (5):

$$J = -D \frac{dC}{dx}$$

where J is the amount of chloride penetrating concrete per unit of area and time, C is the concentration of chloride at different concrete depth (x), and D is diffusion coefficient which depends on the intrinsic property of concrete (w/c ratio, curing time, type of cement). The D coefficient can be calculated if the x-t curve (Fig. 3) is known from the following equation (5):

$$x = 4 \sqrt{Dt}$$

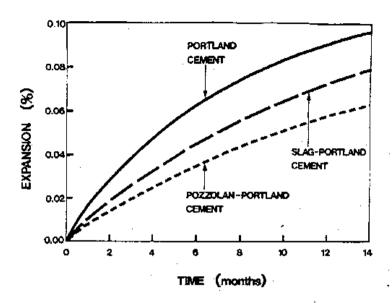


Fig. 2 Change in length of concrete specimens immersed in 10% MgSO4 aqueous solution. Cement factor = 300 kg/m³; w/c = 0.55; slag or type F fly ash used in blended cements in the amount of 20%; curing before sulfate attack = 28 days.

The D diffusion coefficient at a given water/cement ratio (0.55) and at curing time of 28 days is shown in Table 2 for concrete mixes containing portland cement or portland blended cements. Table 2 indicates that the chloride diffusion coefficient of pozzolan cement concrete or slag cement concrete is about 30 or 50% respectively by the D value of portland cement concrete.

2.3 Drawbacks of portland blended cements

Concrete with portland blended cements have lower early strength and are more inclined to the risk of carbonation in comparison with concrete containing portland cement (Table 3).

Fig. 3 Chloride penetration in concrete with portland cement or blended, cament; for mix, proportions see Tab 6.

Table 2 Fick's low and chloride diffusion coefficient for concrete mixes of Fig. 3

J = -	J = - D d x		= 4 √Dt
Type of cement	Portland	Slag-Portland (**)	Pozzolan-Portland (***)
D*(mm²/s)	140-6	0.5 · 10 ⁻⁶	0.3 · 10 ⁻⁶

D values calculated from Fig. 3

** 25% of step

*** 25% of type F fly ash

Due to the lower amount of portland cement, which means higher w/c ratio, and because of the relative slowness of pozzolan and slag in reacting with lime and water, early strength of portland blended cement is lower than that of the corresponding concrete with portland cement (Fig. 4).

Table 3 Drawbacks of concretes with portland blended cements in comparison with portland cement concrete

EFFECT	CONCRETE STRUCTURE DRAWBACK		
Lower early strength	Retard in demoulding particularly in cold weather		
Quicker carbonation process	Less protection of steel reinforcement in lean concrete structures exposed to the carbon dioxide of the atmosphere		

However, due to the subsequent reaction of slag or pozzolan, strength at later ages (after 90 days) of concrete with portland blended cements are at the same level as that of concrete with portland cement (Fig. 4).

Carbonation consists in the reaction of the free lime produced by cement hydration and the carbon dioxide of the atmosphere. Therefore carbonation reduces the alkalinity of concrete and thus reduces its effectiveness as a protective medium for the steel reinforcement. Generally carbonation does not penetrate deeply in good quality concrete, with low w/c ratio, adequately consolidated and cured. Only in porous concrete or where the concrete cover is relatively small carbonation could cause steel corrosion. In such a case, the reduction in the free time as a consequence of the pozzolanic reaction, could increase the carbonation rate in the concrete containing slag and in particular fly ash. Figure 5 shows the carbonation process in two lean concrete mixes containing 250 kg/m³ of portland cement or pozzolan-portland cement (25% of fly ash). The penetration depth of CO₂ into the concrete has been determined by the change in colour on the surface of phenolphtalein concrete treated. Concrete with portland cement performs better than pozzolan-portland cement in resisting the CO₂ penetration.

Both the above mentioned drawbacks (Table 3) may be reduced or completely removed by using fly ash addition as shown in section 3.

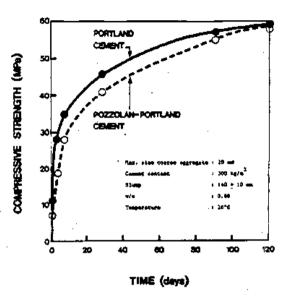


Fig. 4 Compressive strength as a function of curing time for concrete with portland cement or pozzolan-portland cement (20% of type F fly ash).

PRESENT USE AND FUTURE DIRECTIONS OF FLY ASH IN EUROPE

In practice fly ash can be used into concrete in one of the two ways:

- A portland blended cement containing fly ash in place of portland cement is used; such a way of utilization can be carried out by mixing fly ash and portland cement at the cement plant (as discussed in section 2.1) or by replacing a certain part of cement by fly ash at the concrete batching plant; performances of concretes containing fly ash replacing a certain part of cement have been discussed in sections 2.2 and 2.3.

- Fly ash may be introduced as an additional component at the concrete $\ensuremath{\mathsf{mix}}$ plant.

The first alternative has been practised in Europe for the manufacture of slag cement and pozzolan-cement containing natural pozzolan since both slag and natural pozzolan must be ground in the cement mill. The second alternative is gradually developing in Europe with the advent of fly ash which, for its relatively high fineness, does not necessarily need to be ground.

Table 4 shows the percentage of collected fly ash used in cement and concrete at the end of seventies in some European countries when, due to the oil crisis, the coal utilization and thereby the fly ash availability just began to increase. The data of Table 4 indicate that from 10 to 20% of the total available fly ash was devoted to cement or concrete mixes in some European concretes at the end of seventies. These figures should indicate that in Europe the percentage of collected fly ash devoted to concrete constructions was a little higher than the average value of 11.4% estimated by Mans (6) in 1977 for the world-wide production of fly ash (about 280 millions metric tons).

Table 4 Percentage of collected fly ash in cement plants or concrete batching plants in some European countries at the end of 70's.

COUNTRY	% USED	YEAR**
France *	24	1978
Ũ.K.*	19	1978
Poland*	14	1945
Denmark*	14	1981
Germany*	9	1978
Italy	24	1980

* From reference (7); ** 50 to 60% in 1987 (8).

Presently the percentage of collected fly ash devoted to cement or concrete mixes is estimated to be about 50% to 60% in many Western Europe countries. There are some difficulties in using more fly ash than this percentage because in general there are not yet enough warehouses for storing fly ash before distribution to cement or concrete users (8). On the other hand, the use of cement and in particular fly ash are significantly reduced in winter time, just when more coal is used and thereby more fly ash is available. The opposite is true in summer time. This seasonal discrepancy between available and required amounts of fly ash could block the progress in the use of fly ash unless financial investments will be devoted to build fly ash warehouses. Presently the excess of fly ash produced in winter time is devoted to alternative uses such as mine disposal, earth consolidation, etc.

Table 5 shows the expected total production till to 2000 of fly ash (type F and C) as well as of bottom ash in nine West European countries. Type F fly ash is expected to change from 21,8 in 1985 to about 32 million metric tons per year in 2000, whereas there is no substantial change in the amount of type C fly ash mainly produced from lignite. Fly ash could be used as raw material for blended cement or as an additional concrete component, whereas bottom ash because of its coarseness could be advantageously used only in the cement mill to manufacture pozzołan cement.

Table 5 Production (million metric tons/year) of coal ashes expected in European countries* (8)

YEAR	FLY ASH		BOTTOM ASH	
_	Type F	Type C		
1985	22.8	16.6	7.2	
1990	23.4	. 16.7	7.3	
1995	31.1	16.7	8.3	
2000	32.1	16.7	8.4	

Belgium, Denmark, Germany, Finland, Italy, The Netherlands, Spain, Sweden, U.K.

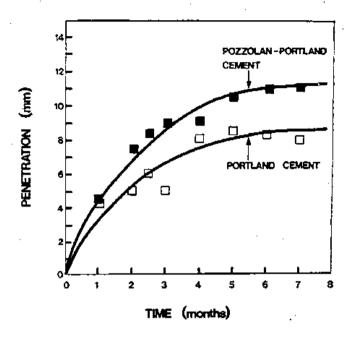


Fig. 5 Penetration of carbon dicode in concrete mixes containing 250 kg/m³ of portland cement or pozzolan-portland cement (20% of type Fifly ash).

After a wet curing of 7 days the specimens were exposed to air (R.H. = 60%).

When fly ash is used as additional component without any reduction in the cement content, the drawbacks consisting in retardation of hardening and acceleration of carbonation (Fig. 4 and 5) can be completely removed.

Table 6 shows the cement content of concrete mixes in the absence or in the presence of fly ash used to replace part of cement or as additional component. By using very small dosage of plasticizer the slump was adjusted at the same level of 140 mm for all the concrete mixes.

Table 6 Mix proportions and setting characteristics of concrete mixes—with or without fly ash (Type F)

Mix No.	Portland cement content (kg/m ³)	Fly ash (kg/m³)	w/c	C+FA	Setting (hr:n Initial	-
1 2 3	300 240 300	50 60	0.60 0.75 0.60	0.60 0.50	4:55 5:15 4:15	7:15 7:45 6:40

The data of Table 6 indicate that fly ash reduces setting time when used as an additional component (Mix No. 3), whereas it extends setting times when it replaces a part of portland cement (Mix No. 2). These data confirm the general Dodson's rule (9) that when setting times are extended by fly ash, the extended setting time is ascribed to the dilution of the portland cement content: according to Dodson, setting time is reduced as the total cement factor (c+FA) is increased (Mix No. 3 in Table 6) and setting time is extended as the w/c ratio is increased (Mix No. 2 in Table 6). However, this rule is by no means general since other chemical factors, such as sulfate and calcium content, as well as water absorption of fly ash, may affect the setting time characteristics.

Data of Fig. 6 are in agreement with those of Table 6 since fly ash increases both early and later strength when it is used as an additional component, whereas fly ash reduces early strength when it is used to replace part of cement.

Similar effects have been found for the carbonation process (Fig. 7). Fly ash reduces the carbonation rate of lean concrete mixes when it is used as an additional component because it reduces concrete permeability. On the other hand, fly ash increases the carbonation rate mainly during the first 3 months when it is used to replace part of the cement in a pozzolan-portland cement because it increases permeability; however, after 3 months the difference in the carbonation rate for portland cement concrete and pozzolan cement concrete is negligible.

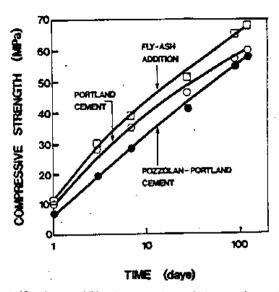


Fig. 6 Effect of fly ash as an additional component or replacing part of cement (pozzoian-portland cement) on concrete compressive strength (see Table 5).

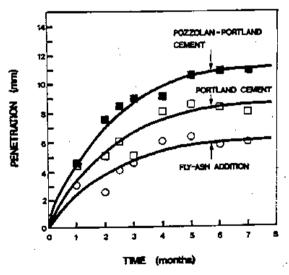


Fig. 7 Effect of fly ash on the CO₂ penetration in lean concrete mixes. Fly ash addition as concrete component = 50 kg/m³. Content of portland cement or pozzolan-portland cement (20% fly ash) = 250 kg/m³. After a wet curing of 7 days the speckmens were exposed to air (R.H. = 60%).

4. PRESENT USE AND FUTURE DIRECTIONS OF SILICA FUME IN EUROPE

Last but not least, silica fume was studied in Europe, for the first time in the world, as concrete mineral admixture in the early 50's at the Norwegian Institute of Technology (10). In the mid 70's the use of silica fume both in practice and in laboratory started in several Scandinavian countries; Norway, Sweden, Denmark and Iceland (9). After then, research work and practical use of silica fume in concrete started in many countries outside Europe.

Presently Norway and U.S.S.R. are among the biggest silica furne producers. Lower amounts of silica furne are also available in other European countries such as France, Germany, Italy, etc.

There are many interesting reports (10-16) on the excellent performances of silica furne as pozzolanic material which are not discussed here.

In the present report only some specific aspects concerning the future use of silica fume are examined.

First of all, the total available amount of silica fume is very small in comparison with other pozzolanic materials such as fly ash or slag. Jahren (14) estimates that much less than 1 million metric ton per year is available in the Western World and Japan.

Due to the high market request, the silica fume price is relatively high, i.e. 2 to 3 times the cement price. This means that silica fume will be devoted in the future to special cement mixes such as repairing and grouting premixed mortars, or very-high quality special concretes where high strength and long-term durability are required. Moreover, as silica fume does not perform very well when used alone, due to very high water requirement, for the above mentioned specials application silica fume must be used in combination with superplasticizer used at very high dosage (2-6% by weight of cement). Therefore the additional extra-cost for superplasticizer will make even more silica fume a very special pozzolanic admixture.

In view of these future directions, the author of present report thinks that the following three technical aspects should be investigated:

- a) thixotropic behaviour of cement mixes;
- b) brittleness of high-strength concretes;
- c) crack sensitivity

4.1 Thixotropic behaviour of cement mixes

When fresh mortar and concrete are sprayed on an old concrete structure the sagging effect could be reduced or completely removed by increasing the thixotropy of the sprayed cement mix. Such a technique is practised in Europe to spray high quality cement mixes to repair deteriorated concrete structures without using set accelerating admixtures, which could damage the long-term durability of the repairing mortar or concrete.

The combined addition of silica tume and superplasticizer is advantageously used to obtain very thixotropic cement mixes which are pumpable and sprayable even at very low w/c ratio and at the same time do not sag just after spraying.

The evaluation of the thixotropic characteristics could be carried out by examining the rheological properties of cement mixes. Figure 8 shows the shear stress (τ) -shear rate (D) curve for: plain cement mix (A); superplasticized cement mix (B); cement mix with silica tume (C); and cement mix with superplasticizer (4%) and silica tume (D).

In the presence of silica fume alone (Fig. 8-C), the mix appears cohesive but very stiff even with a w/c ratio of 0.55. This corresponds to a very high value in the yield stress and a relatively large hysteresis loop value between the upcurve and the downcurve. With the combined addition of superplasticizer and silica fume the w/c ratio is reduced from 0.55 to 0.38. This mix appears again cohesive and sticky and, at the same time, very flowable. In comparison with the plain mix (Fig. 8-A) or that with superplasticizer alone (Fig. 8-B), the cement mix containing both superplasticizer and silica fume (Fig. 8-D) shows a higher yield stress and a larger hysteresis loop as a consequence of the thixotropic beahaviour.

4.2 Brittleness of high-strength concretes

Even if silica fume by itself does not cause any significant change in ductility of concrete (10), high strength concrete - including superplasticized concrete in the presence of silica fume - behaves as a brittle material. However, a brittle material does not necessarily mean a brittle construction since design and reinforcement could completely transform a brittle structure into a ductile one.

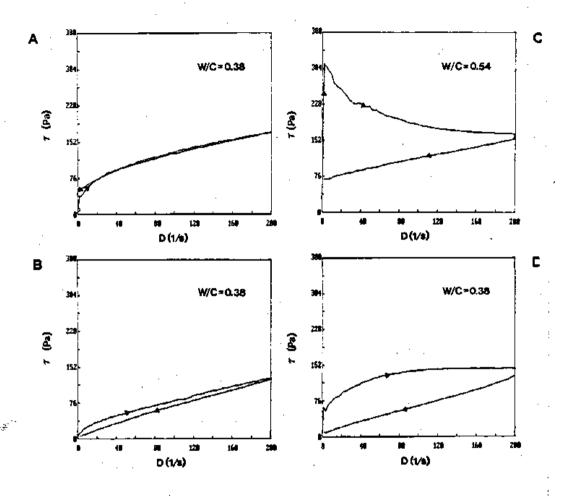


Fig. 8 Shear stress (τ) Versus shear rate (D) for cement paste (A); superplasticized cement paste (8), cement paste with silica fume (C), and superplasticized cement paste with silica fume.

Stress-strain tests have been carried out on normal-strength concrete (40 MPa) and high strength concrete (80 MPa) containing both superplasticizer (4%) and silica fume (15%). Cyclic loading tests have been carried out at constant strain rates in the reloading and unloading curves (Fig. 9 to 11). Figure 9, illustrates the relatively ductile behaviour of the normal-strength concrete specimen, whereas Fig. 10 shows the brittleness of the high-strength concrete specimen since the falling part of the stress-strain curve is much steeper. However when reinforced, the high-strength concrete becomes a very ductile material (Fig. 11).

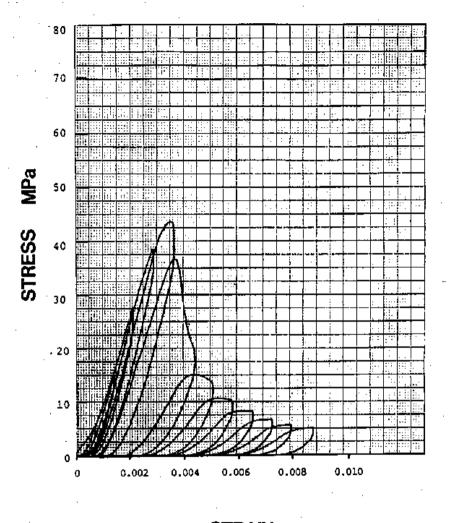
Since high-strength concrete containing silica fume is generally devoted only to reinforced structures, research on proper design and adequate reinforcement should be encouraged to utilize the potential properties of silica fume high-strength concretes.

4.3 Crack sensitivity

In general, silica fume cement mixes have a higher shrinkage potential than control cement mixes (10). The effect is more evident in paste (17) or mortar (18) specimens particularly at higher content of silica fume (above 10%). Shrinkage data (10,18, 19) of concrete are more difficult to evaluate and contradictory results have also been obtained (10).

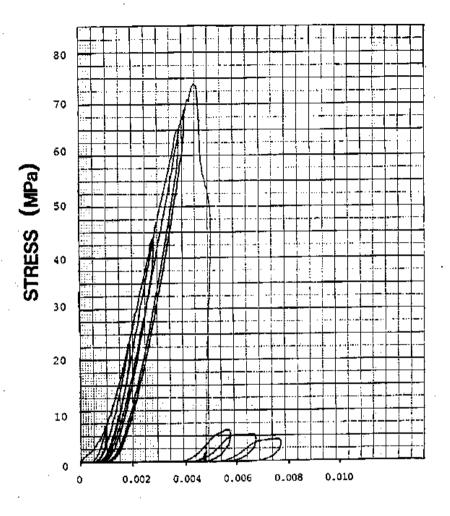
Johansen found that silica furne makes concrete vulnerable to cracks caused by both plastic (20) and drying shrinkage (18).

Experiments carried out by Chatterli, Collepardi, and Moriconi (21) demonstrate that mixing procedure affects significantly the crack formation in the presence of silica fume. When cement and silica fume were normally mixed with water, cracks appeared within 24 hr after casting even though the specimens were still in their moulds and in a humid atmosphere. When silica fume was first mixed with water and then portland cement was added to the silica fume slurry, no crack was visible until the specimens were exposed to a drying atmosphere. Therefore, it seems that, in the absence of a preliminary wetting, silica fume may absorb water from the cement paste causing an "inside" drying shrinkage and than visible cracks even in a humid atmosphere.



STRAIN

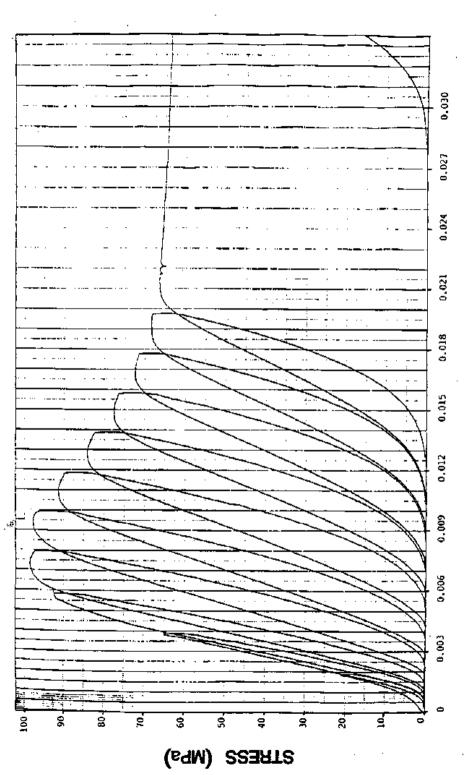
Fig. 9 Stress-strain cycling loading test on normal strength concrete (40 MPa).



STRAIN

Fig. 10 Stress strain cycling loading test on high-strength concrete (80 MPa).





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STRAIN

To explain such a crack sensivity and in particular the effect of the mixing procedure, a new model for silica fume morphology may be proposed. According to the particle size measurements, silica fume appears in form of very fine particles from 0.01 to 1 micron with an average value 0.1 micron. According to the SEM micrographs silica fume appears in form of bigger aggregates up to 30 microns (Fig. 12) or even more. Presently, it is assumed that the 0.1 micron particles should form the bigger aggregates by "weak" solid-to-solid contact bonds ("Individual Grapes" model).

An alternative model ("Bunch of Grapes" model) is here proposed by the author of the present report. According to this new model, among the very fine silica fume particles (0.1 micron) there are also relatively "strong" vetrified bonds forming the bigger aggregates observed by SEM (Fig. 12).



ig. 12 SEM micrograph of silica fume

The relatively high BET specific surface area of silica fume, determined by N_2 adsorption (15 to 30 m²/g), is in agreement with both the "Bunch of Grapes" model and the "Individual Grapes" model, Indeed, even for the new model, the specific surface area should be very high to the fact that N_2 molecules can penetrate the interstitial voids among the individual silica fume particles.

The "Bunch of Grapes" model could explain why silica furne could cause cracks in cement mixes even in a humid atmosphere. Part of mixing water could leave the cement paste and penetrate the interstitial voids among the individual silica furne particles of the "Bunch of Grapes" microstructure. On the other hand, a careful preliminary mixing of silica furne with water should saturate the silica furne microstructure and remove the crack sensitivity drawback of cement mixes containing silica furne.

If the above mechanism is "correct", this should not be in agreement with the particle size measurements (0.01 to 1 micron) found in the literature (15). Really the author of the present report was never able to reproduce these particle size results by analyzing many silica fume from different sources. Figure 13 illustrates the particle size distribution by using a laser size analyzer after dispersing the pulverized sample of silica fume in water by ultrasonic pulses. The particle size distribution up to 100 micron (Fig. 13) is in agreement with both the SEM micrograph (Fig. 12) and the "Bunch of Grapes" model.

More research is needed to explain the discrepancy in the particle size distribution between the results of the present report (Fig. 13) and those found in the technical literature (15).

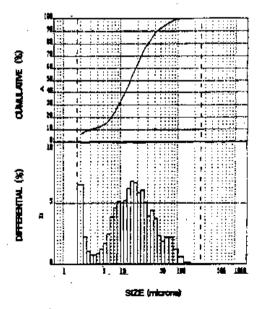


Fig. 13 Particle size distribution of silica fume: cumulative (A) and differential (B).

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