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Chemical admixtures enhance effectiveness of supplementary cementing materials in concrete

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Concrete today is recycled, placed faster, transported to higher locations and used under cold and hot arid conditions because of the continued evolution of chemical admixtures. The new generation of admixtures affords designers and contractors more control over the properties they want in a concrete mix. Current concerns over salt damage to concrete, the alkali-aggregate reaction, the need to produce more durable structures, make some admixtures more topical than others. For these reasons, chemical admixtures such as superplasticisers and supplementary cementing materials such as silica fume and fly ash are the subject of increased interest. The combined use of these materials produces synergistic effects which result in a range of modifications enabling highly durable concretes to be placed under a variety of conditions.

Pozzolanic and other hydraulic cementitious materials are added as a partial replacement of cement not only to achieve economy but also to obtain specific engineering properties in the finished product. A well proportioned mixture generally shows improved mobility, cohesiveness, ultimate strength and durability[1-6].

It is possible to achieve the required workability without strength reduction at early ages with replacement levels of 15-20 percent or 6-8 percent by weight fly ash or silica fume, respectively[7]. Higher substitutions lead to pronounced thixotropic effects, lower strengths and higher drying shrinkage. The use of increased levels of fly ash therefore, will require some method of offsetting such constraints. Previous work[8-11] shows that the use of admixtures in mixes containing fly ash and silica fume affords a method of overcoming the slow rate of strength gain at early ages, improving rheology and durability. It is now possible to produce high strength concrete with higher strengths at early ages using large percentages of fly ash and superplasticisers[12]. Ultra high strength concretes of 150 MPa at 28 days[12] have been developed using silica fume and superplasticisers.

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The role that admixtures play in augmenting the desired features in fly ash or silica fume/Portland cement mixes is described; specific applications are cited to illustrate the manner in which admixtures offset limitations and increase the effectiveness of the two supplementary cementing materials.

Role of admixtures

Rheological properties

Admixtures modify rheological behaviour and improve the quality of plastic concrete, for example, increased workability, or water reduction at given consistencies, improved finishing qualities, controlled bleeding and segregation.

Effects on plastic properties : Replacement of small amounts of cement by fly ash generally improves the workability of concrete and reduces water demand. The improvement is postulated to result from better packing and the "ball bearing" effect produced by the spherical fly ash particles. Addition of these materials to the mix reportedly reduces the mean free space for water by increasing the total surface area and reducing sedimentation[10]. Consequently, internal friction due to particle-particle contact in the aggregate is decreased without increasing viscosity. High carbon fly ashes and some Type-C fly ashes, however, may cause workability problems even at

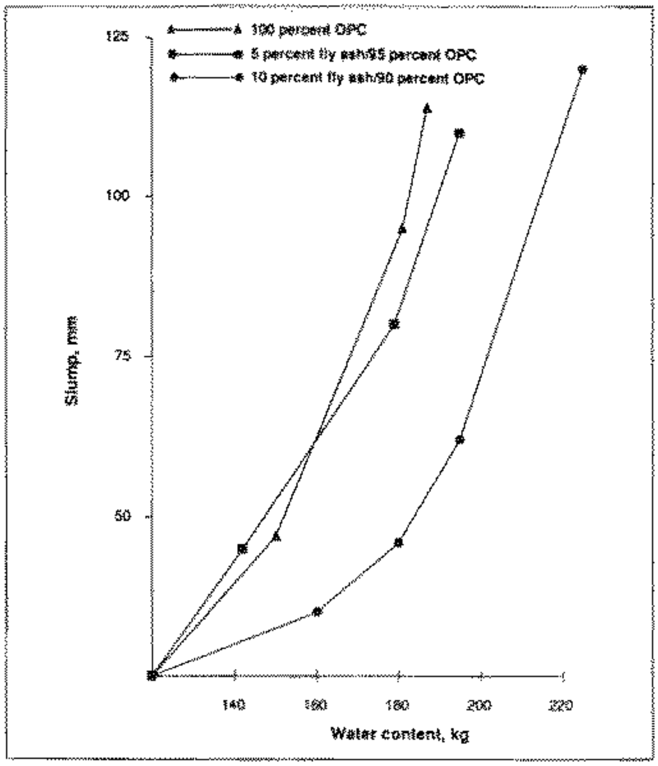

Fig 1 Effect of cement replacement level on the water demand and slump of fly ash Portland cement concrete (350 kg cement concrete mix)

low (5-10 percent) replacement levels [14]. A higher water demand than that required by a 100 percent Type-1 cement mix may be observed at a given slump value, *Fig* 1. This has been attributed to the increased levels of ettringite formed in fly ash/Portland cement mixes. Ettringite crystals have a higher affinity for water and, therefore, increase the water demand[16]. At higher cement replacement levels, however, the effect is generally masked by the lubricating effect produced by the increased number of spherical particles. Much improvement in water reduction and in workability in blended mixes can be provided through the use of a superplasticiser. The admixture reduces the rate of formation of ettringite[16], and the inherent high cohesion by greater dispersion of the fine particles.

Medium cement-content mixes produce highly cohesive concrete at cement replacement levels exceeding 10 percent fly ash and 4 percent silica fume, by weight of cement. As a result, the incidence of "bug hole" formation in precast products, and finishing problems such as "stickiness" due to frictional drag on finishing tools is increased. Admixtures can alleviate such problems by increasing the dispersion of the particles. The effect of the dispersing action is seen in the change in viscosity observed in cement/fly ash and cement/silica fume paste, *Figs* 2 and 3. The reduction in yield value and plastic viscosity makes the mix more responsive to vibratory compaction causing entrapped water to be driven to the surface or the periphery of the concrete effectively reducing "bug holing". Frictional drag on the finishing tools is reduced due to the presence of some free water in the mix providing a "slickness" on the trowel. Use of silica fume in superplasticised flowing concrete enables the production of cohesive concretes of very high mobility. Thus, the synergistic effects produced by the interaction of silica fume with the superplasticiser afford flowing mixes which remain cohesive without segregation. This is rarely possible when the materials are used individually.

Pumping of fly ash or silica fume/Portland cement mixes : Successful pumping of concrete requires two basic mix properties:

- *(i)* sufficient paste content to form an annular grout film against the pipe wall to act as a slip surface
- *(ii)* suitable grout consistency and interstitial void structure to offer good resistance to the forced bleeding of water from the cement paste and prevention of dewatering under pressure.

Silica fume increases the viscosity of the cement paste and also influences the void structure by acting as a pore filler. Conventional water reducing admixtures or superplasticisers augment the "pumping aid" action of silica fume by increasing thixotropy, but allowing ready mobility due to shear thinning effects. Such benefit is best realised in lean or harsh mixes where low paste content or poor shape, texture and gradation of the available aggregate makes it difficult to pump concrete.

Improvements to the quality of hardened concrete

Improvements to the quality of hardened fly ash and silica fume concrete such as increased long term strength, uniformity, decreased permeability and absorption, and increased abrasion resistance are realised when admixtures are used.

Maintenance of uniformity in fly ash/Portland cement mixtures : The variability of fly ashes (both types C and F) is well documented[14]. There is often a wide range in chemical composition between fly ashes from different sources, *Table* 1. The

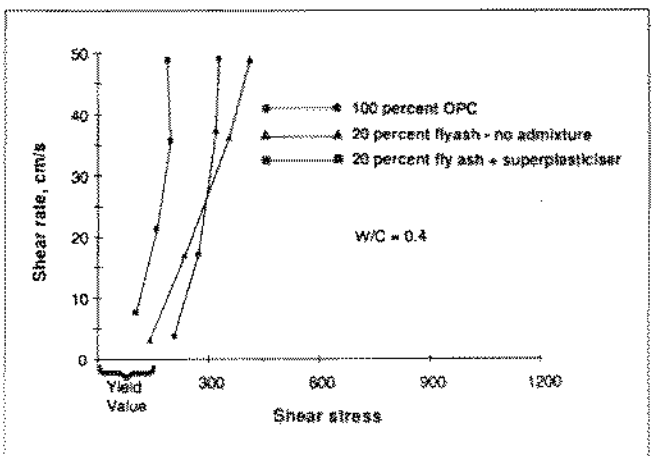

Fig 2 Shear stress/shear rate relationship for cement/fly ash paste with and without admixtures

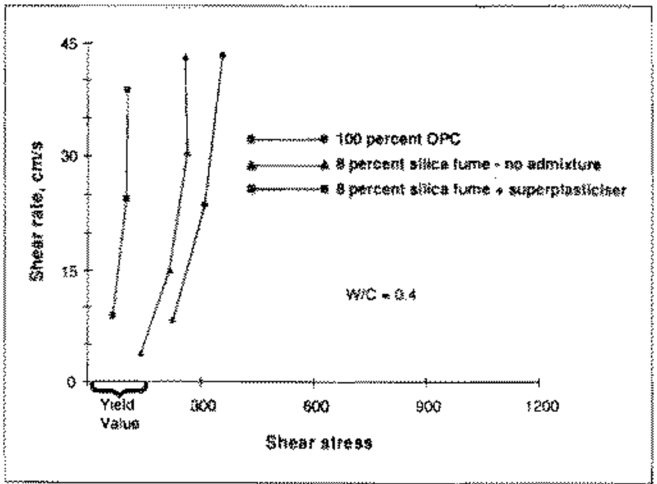

Fig 3 Shear stress/shear rate relationship for cement/silica fume paste with and without admixtures

range of chemical composition within a given fly ash source, although fairly small, may still cause variations in performance. Admixtures play a significant role in maintaining the consistency of the specified concrete mix properties by ensuring a reduced standard deviation in compressive strength values through the closer control of water content and slump, *Fig* 4.

Durability : One of the most dramatic improvements that results from the use of silica fume and fly ash is the durability of the hardened concrete. When used in conjunction with admixtures, both silica fume and fly ash significantly improve properties such as permeability, abrasion, sulphate resistance, freeze-thaw resistance and reduced alkali-aggregate reaction.

A number of workers[18-22] have shown that the pore size range of hardened silica fume or fly ash concrete is significantly shifted to the smaller sizes. Permeability is further reduced when these materials are used with superplasticisers[22] and dense concrete bodies are produced. Consequently, permeability to water and injurious chemicals is drastically reduced and its susceptibility to freeze-thaw damage and scaling diminished. Advantages obtained from the increased density are reflected in improved resistance to abrasion and shock-impact stresses in warehouse floors and roll-on and roll-off docks, respectively.

Dense superplasticised fly-ash or silica fume concrete is well suited for use in structures such as water retaining towers and in breakwater applications where both sulphate attack and abrasion and erosion are experienced at the tidal zones. Sulphate resisting cement is typically used in marine environments where the concrete is required to withstand sulphate and chloride attack. However, it is possible to obtain sulphate resisting properties with fly ash/Portland cement mixes when a 30 percent cement replacement is used in conjunction with a superplasticiser[22].

The effect of fly ash and silica fume on the alkali-aggregate reaction has been well-reported[1, 21, 23]. Greater stability of the concrete can be ensured by the use of a water-reducing admixture which affords the benefits of the use of silica fume ; but at much reduced water contents than concretes which contain no admixtures. The greater water demand of silica fume is therefore offset allowing for reduced moisture levels in the hardened concrete.

Special concretes

Various classes of admixtures facilitate design and construction techniques not readily practicable without such materials. The following examples illustrate the important functions admixtures play in modifying fly ash and silica fume concrete to meet the specific requirements of special applications.

Shotcrete : Shotcrete is a process by which concrete is sprayed on to a surface under pressure. The sprayed material is expected to stay in place on vertical and overhead surfaces, and this is usually effected by acceleration of the set-time to within 5 to 10 minutes. This results in a 20-30 percent strength loss. Admixtures used in shotcrete usually fall into four categories:

(i) air entraining agents
(ii) accelerators
(iii) retarders
(iv) finely divided inert or hydraulic reactive solids.

Table 1: Ranges in chemical composition of lignite and bituminous coal ashes (weight in percentages)[14]

Reference	*Silicon oxide*	*Alumina*	*Ferric oxide*	*Calcium oxide*	*Magnesium oxide*	*Sulphur trioxide*	*Alkalies*	*Carbon*
Bituminous								
Product 1	34-52	13-31	6-25	1-12	0.5-3	0-2	0-2	1-12
Product 2	25-52	14-30	4-31	3-8	0.5-3	0.3-3	0.5-5	1-19
Product 3	40-55	25-35	5-24	0.5-4	0.5-5	0.5-5	0.7-4	0.5-12
Lignite								
Product 1	15-52	8-25	2-9	11-36	2-11	0.7-27	0-7	1-12
Product 2	24-43	12-21	5-14	18-41	4-10	0.7-2.5	0.5-5	1-4
Product 3	20-40	10-30	3-10	10-32	0.5-8	1-8	1-8	0.5-2

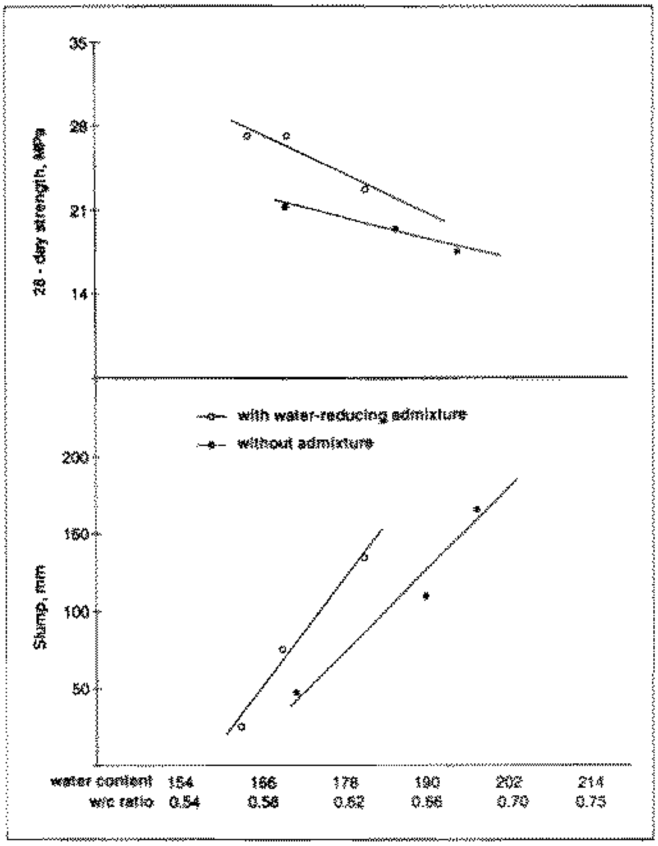

Fig 4 Influence of water--reducing admixture on water content, slump, and water-cement ratio

Silica fume which falls under category *(iv)* is quite suitable for this application, a method of providing the required mix characteristics (of high cohesion and rapid setting to prevent sloughing off from vertical surfaces) without the attendant 20-30 percent strength loss that occurs with traditional accelerators[24]. It is now possible to use additions of silica fume in conjunction with superplasticisers in shotcrete mixes which give reduced rebound levels, good dense layers with only a marginal strength reduction in comparison with normal concrete mixes.

Mass concrete : Perhaps, the most widely-known application of fly ash has been in mass concrete, where it is used to reduce the heat evolved in huge placements. Even with replacements in the range of 50 percent, damaging peak temperatures often result. One method of reducing the heat evolved is by the use of admixtures. Although water-reducing retarders do not reduce the total amount of heat evolved, they delay and spread the heat generated over an extended period[6]. They also facilitate higher cement replacement levels (60-75 percent) by ensuring that specified strengths are achieved[1,12]. Thus, further reduction in the total amount of heat generated can be achieved.

Underwater concrete : Fly ash has been used in underwater concrete to increase the cohesiveness of the mix and prevent cement "wash-out". More recently, the "structured" consistency afforded by silica fume incorporation has given mixes which are quite suited for tremie concrete[6,25]. When used in conjunction with superplasticisers and anti-washout admixtures, the "gel like" consistency of the mix shows little tendency for cement "wash out" and spreads in a wider circumference than that given by fly ash/cement mixes when it drops from the pipe. Consequently, tremie pipe spacing and pour time is reduced.

Table 2 : Water reduction using a superplasticiser (360 kg cement/40 kg fly ash mix)

Admixture dosage	W/C ratio	Water reduction, percent	Slump, mm	Cement reduction, percent	Compressive strength, MPa	
					1 day	7 day
0	0.55	0	55	-	18	24.9
Normal	0.48	13	65-70	5	21	30.6
2X Normal	0.44	20	75-80	10	24	32.3
3X Normal	0.39	28	80-100	15	22	34.7

High strength concrete : Aggregate-cement bond and matrix strength play a significant role in determining the strength of high strength concrete. The high cement contents that are generally required for such mixes are often counter-productive since the resultant high shrinkage stresses cause loss of aggregate-cement bond or cracking of the cement paste. Matrix strength is primarily dependent on matrix porosity, which is governed by the water-cement ratio and efficacy of packing. Admixtures can be used to effect cement and water content reductions (without decreasing strength) and improve packing, *Table* 2. The importance of compaction produced with the help of admixtures, fly ash and silica fume is well documented[12,23,26]. The work of Birchall and Mukherjee[26,12] showed

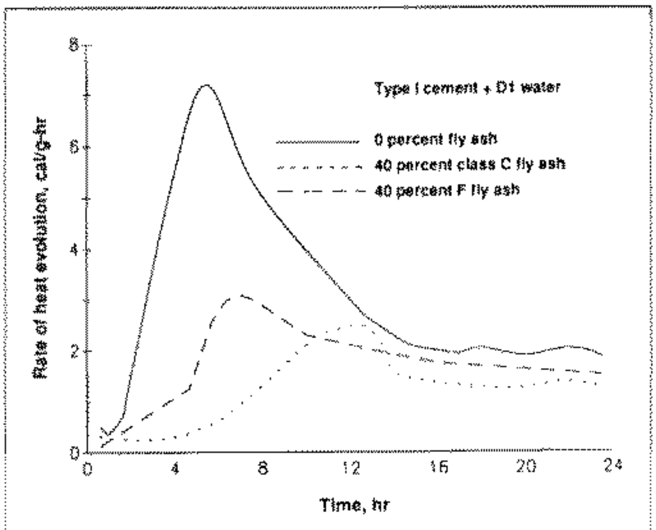

Fig 5 Rate of heat evolution of pure cement and fly ash/cement blends

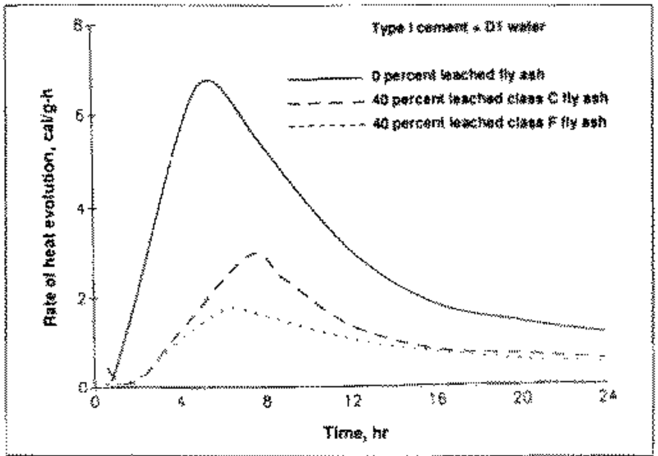

Fig 6 Rate of heat evolution of pure cement and previously leached fly ash/cement blends

that remarkably high flexural strengths can be obtained by the blending of cementitious materials and control of rheological properties of pastes with low water-cement ratios. Very high strengths have also been reported when silica fume is blended with cement in the presence of a superplasticiser[13].

Economic considerations

The chief use of admixtures in most ready-mix and precast operations is to reduce the cost of concreting operations by effecting a reduction of the overall cost of concrete ingredients, permitting rapid mould turn-over and ease of placing and finishing. The following applications show how they function in fly ash or silica fume concrete to obtain these objectives.

Improved early strength development : The strength development of concrete containing fly ash depends on the mix proportioning and on the type of ash used in the mix. When it is used in concrete in the classical manner, that is, as direct replacement for cement, the strength gain at early ages is slower than that for control concretes. This retarding effect is accentuated at lower temperatures. However, fly ash concrete whose strength at early ages is comparable with that of control concrete (using 100 percent Portland cement) can be made using admixtures.

The reduced rate of hydration of Portland cement/fly ash mixes has been attributed to the retarding effect of fly ash on the hydration of C_3S[15], C_3A and C_4AF phases of Portland cement[27,28]. Other work[29] has shown that the retardation may also be related to the condition of the fly ash surfaces. This is demonstrated in the heat evolution curves obtained by the investigators for samples of fly ash as received and on materials previously leached prior to blending with cement, *Figs* 5 and 6. The rate of heat evolution of pure cement and fly ash mixtures hydrated in de-ionised water at 38°C is shown in *Fig* 5. The data shows that both class-C and class-F fly ash retard cement hydration. The major peak is delayed and the amount of heat evolved (peak size) in the fly ash containing mixtures is diminished relative to that of the pure cement paste. In *Fig* 6, the rates of heat evolution of mixtures of leached fly ashes under the same conditions as above is compared. The data indicate that the class-C and class-F leachates still retard hydration of cement but, that the rate of the reaction of the class-F fly ash has been influenced by leaching[29].

The role of an admixture in improving rate of strength gain of fly ash/cement concretes at very early ages may also be that of improving the surface condition of the fly ash particle, enhancing its ability to react with the surrounding liquor. Other strength accelerating effects produced by admixtures include the following:

- *(i)* an increased rate of hydration due to the high degree of deflocculation of the cementing particles, resulting in more rapid $Ca(OH)_2$ production and promotion of the pozzolanic reaction
- *(ii)* an autocatalytic effect due to higher peak temperatures generated during hydration at low water-cement ratios. The low water-cement ratio influences the hydration kinetics by causing a greater absorption of the admixture by the cement grains
- *(iii)* a reduction in the amount of freezable water during hydration at lower temperatures
- *(iv)* improved compaction due to the improved particle packing.

Increased use of type-F fly ashes : Due to the higher carbon content and lower pozzolanic activity of type F fly ashes, their use in normal concrete is more limited than the higher *CaO* containing type C fly ashes. Often, the percentage replacement is kept to levels below 10 percent, due to the slow strength development and higher water demand. The use of a superplasticiser will significantly reduce the water demand and promote early strength gain. The improved deflocculation of cement agglomerates produces an increased rate of $Ca(OH)_2$ generation which stimulates pozzolanic activity in the fly ash. The superplasticiser, therefore, facilitates a greater use of type-F particularly in areas where bituminous coal is used.

Conclusion

The above examples clearly demonstrate that modifications to the interparticle forces in the cementitious paste by admixtures influences both the hydration and packing efficiency in fly ash or silica fume concrete. This produces significant improvements in rheological, structural and durability characteristics of the concrete which are not readily realised when the materials are used individually. They enable concrete containing fly ash or silica fume to be transported farther, placed faster and increase its ability to remain functional in the intended service environment.

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