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Analysis of Admixtures and Their Effects of Silica Fumes, Metakaolin and PFA on the Air Content

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Abstract: *This paper presents a review of the properties of fresh concrete including workability, heat of hydration, setting time, bleeding, and reactivity by using mineral admixtures fly ash (FA), silica fume (SF), ground granulated blast furnace slag (GGBS), metakaolin (MK), and rice husk ash (RHA). Comparison of normal and high strength concrete in which cement has been partially supplemented by mineral admixture has been considered. It has been concluded that mineral admixtures may be categorized into two groups: chemically active mineral admixtures and microfiller mineral admixtures. Chemically active mineral admixtures decrease workability and setting time of concrete but increase the heat of hydration and reactivity. On the other hand, micro filler mineral admixtures increase workability and setting time of concrete but decrease the heat of hydration and reactivity. In general, small particle size and higher specific surface area of mineral admixture are favourable to produce highly dense and impermeable concrete; however, they cause low workability and demand more water which may be offset by adding effective super plasticizer.*

Keywords: *Silica Fume (SF), Metakaolin (MK), Fly Ash (FA), Ground Granulated Blast Furnace* Slag

1. Introduction

The raw materials needed for the manufacture of Portland cement (PC) are available in most parts of the world, and the energy requirements for its production may be considered to be relatively modest. Nevertheless the use of alternative binders or cement replacement materials, has become a necessity for the construction industry because of the economic, environmental and technological benefits derived from their use. Furthermore recent years have seen increased concerns regarding the depletion of raw materials, energy demands and the consequent environmental damage. These concerns have led to wider utilization of existing cement replacement materials and further search for other less energy intensive materials. Many of these mineral admixtures are industrial by-products, and are considered as waste. When used as a partial cement replacement material, typically in the range of 20 to 60% by mass, the energy and cost savings are substantial. From an environmental point of view mineral admixtures are playing an undisputed role. They are responsible for substantial "environmental unloading" because their disposal can be hazardous to the environment and higher utilisation of them can result in reduction of greenhouse gas emissions attributed to the cement industry. Two of the revolutionary developments in concrete technology in the last century have been produced by air entraining agents (AEAs) and superplasticizers. Superplasticizers or high range water reducing admixtures (HRWRAs) are concrete admixtures which can be mainly used either to increase the workability of fresh concrete at a given mix composition or to reduce the amount of mixing water and water/cement (w/c) ratio for a given workability in order to increase strength and durability. For instance to compensate for the loss of workability in mixes like those containing pozzolanic materials such as condensed silica fume (CSF) and metakaolin (MK) or even increase the water reduction effect of pulverized fuel ash (PFA) and ground granulated blast furnace slag (GGBS) we normally use superplasticizers. Due to addition of superplasticizers the slump increase at a given mix composition can be 150-200 mm and the reduction of mixing water at a given slump can be up to 30%, both depending on the method of addition, dosage and type of admixture used. Presently the most important HRWRAs available are based on condensed melamine sulfonated formaldehyde (MSF) or naphtalene sulfonated formaldehyde (NSF) in the form of 40% aqueous solution to facilitate an accurate, reliable and automatic dispensing at the batching plant. The optimum dosage of commercial superplasticizers is in general in the range 1- 2% by mass of cement. The main action of the molecules of such superpalsticizers is to wrap themselves around the cement particles and give them a highly negative charge so that they repel each other. This results in deflocculation and dispersion of cement particles with the resulting improvement in workability.

Air entraining agents are admixtures which are capable of forming air bubbles dispersed throughout the cement matrix that binds the aggregates. After compaction, normal concrete is likely to contain about 1-2% air by volume, this accidentally entrapped air being unevenly distributed and consisting of bubbles of irregular size and shape. Air entraining agents introduce a controlled amount of air in the form of millions of bubbles of uniform size and uniformly distributed throughout the concrete mix. There is another distinctive difference between air voids accidentally entrapped in concrete and the deliberately entrained air bubbles. The latter are very much smaller, typically 50 m in diameter whereas the former can be as large as the familiar, albeit undesirable, pockmarks on the formed surface of concrete. Numerous types of air entraining agents are commercially available with the vinsol resin based products being the most common ones. The optimum dosage for AEAs is usually below 1% by mass of cement.

The presence of entrained air in fresh concrete has a pronounced effect on its properties. One of these is workability, which is improved. For adequate workability, the aggregate particles must be spaced in a way that they can move past one another with relative ease during mixing and placing. In this respect, the entrained air voids are often thought of as millions of tiny ball bearings in the concrete, making the mix more workable. Entrained air also eliminates or minimises segregation and subsequent bleeding. Although there are also other advantages to be realised, the principal reason behind the use of air entrainment agents is the improvement that they impart to the concrete's resistance to frost action and to its deterioration due to repeated freezing and thawing. A given volume of air and an appropriate spacing factor are required to produce an adequate air bubbles system to protect concrete from freezing and thawing. Because the damaging action of freezing and thawing involves expansion of water on freezing and associated osmotic processes, it is logical to expect that, if excess water can readily escape into adjacent air-filled voids, damage to the concrete will not occur. This is the underlying principle of improved frost resistance by air entrainment.

II. Admixture

2.1 CHEMICAL ADMIXTURES FOR CONCRETE

Definition: what are chemical admixtures?

The definition of RILEM (International Union of Testing and Research Laboratories for Materials and Structures) is:

- Admixtures for concrete, mortar or paste are inorganic or organic materials
- These are added to the normal components of a mix not normally exceeding 5% by mass of cement or cementitious materials

Why admixtures? The need.

- If we are pouring a low grade concrete, say M20, If we are not unduly concerned about its water content nor its water-cement ratio,
- If the cost of materials and labour are paid entirely by the owner (or some one else) at whatever rates we have quoted, then, Admixtures will make the concrete more expensive. But then our concrete will be an *indifferent* one,

How do they act?

- The chemical, physical or physio-chemical actions of admixtures in cement concrete are quite complex.
- In fact, cement itself is an extremely complex compound with major compounds such as calcium silicates, calcium aluminates, gypsum.
- Besides it contains many alkali and other calcium salts.
- The action of admixtures can, however, be simplified for the sake of Understanding, as:

(i) adsorption

(ii) De-flocculation or dispersion

(iii)Chemical absorption or interaction

Often, all the three take place. We should know a little about these so that we can choose admixtures for our job more correctly

2.2 PHYSICO-CHEMICAL ACTIONS OF ADMIXTURES

The most important compounds of cement that react very early when water is added are:

- Tricalcium silicate (C3S), and
- Tricalcium Aluminate (C3A)

III. Silica fume, Metakaolin,

PULVERISED FUEL ASH (PFA)

3.1 SILICA FUME

Silica fume (SF) is a byproduct of the smelting process in the silicon and ferrosilicon industry. The reduction of high-purity quartz to silicon at temperatures up to 2,000_C produces SiO2 vapours, which oxidizes and condense in the low temperature zone to tiny particles consisting of non-crystalline silica. (Fig.3.1)

Fig. 3.1 Silica fume

Properties of Silica Fume

Physical Properties

Silica fume particles are extremely small, with more than 95% of the particles finer than 1 lm. Its typical physical properties are given in Table.3.1 & Fig.3.2. Silica fume colour is either premium white or grey.

Chemical Composition

Silica fume is composed primarily of pure silica in non-crystalline form. X-ray diffraction analysis of different silica fumes reveals that material is essentially vitreous silica, mainly of cristobalite form. Silica fume has a very high content of amorphous silicon dioxide and consists of very fine spherical particles.

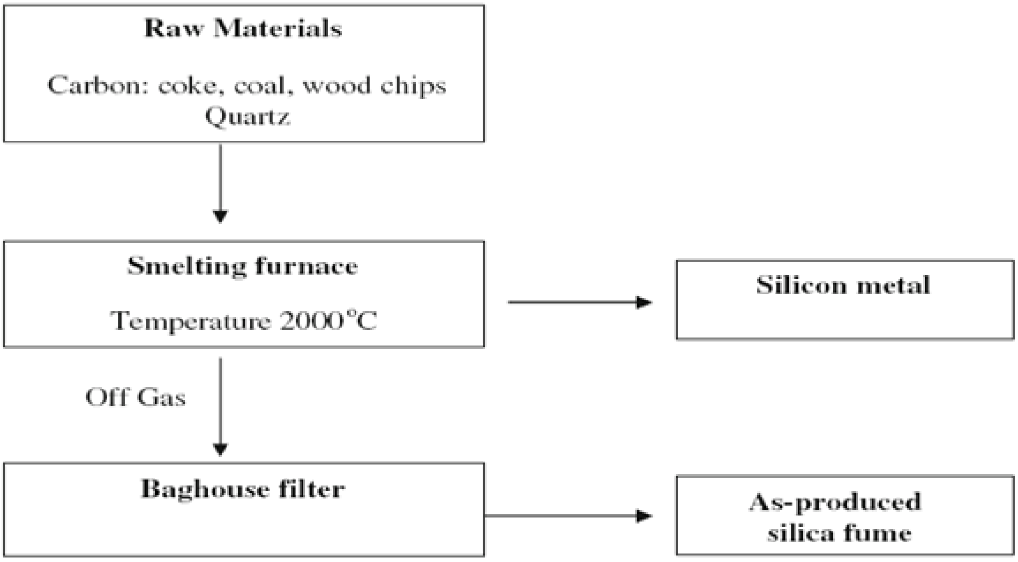
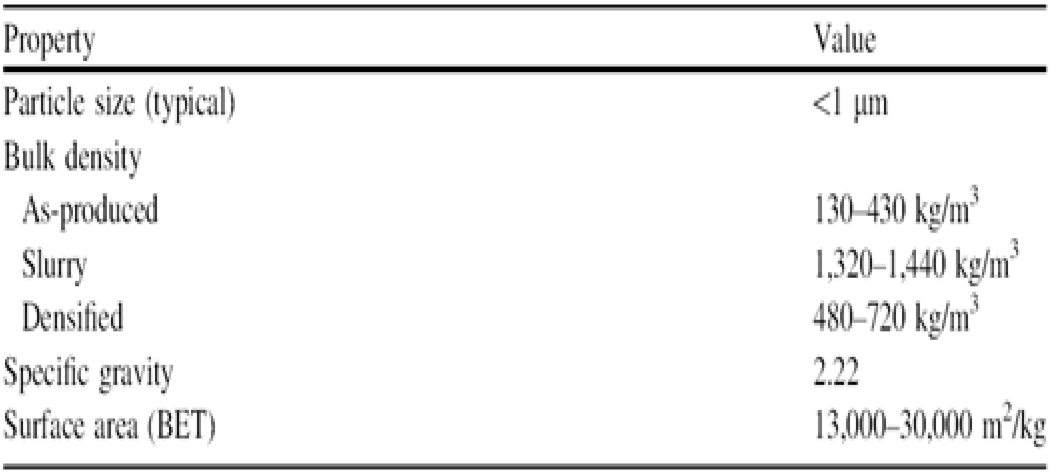


Fig. 3.2 Schematic diagram of silica fume production



Property	Value
Particle size (typical)	<1 μm
Bulk density	
As-produced	130–430 kg/m^3
Slurry	1,320–1,440 kg/m^3
Densified	480–720 kg/m^3
Specific gravity	2.22
Surface area (BET)	13,000–30,000 m^2/kg

Table 3.1 Typical physical properties of silica fume

3.2 METAKAOLIN

What is metakaolin?

Metakaolin is refined kaolin clay that is fired (calcined) under carefully controlled conditions to create an amorphous aluminosilicate that is reactive in concrete. Like other pozzolans (fly ash and silica fume are two common pozzolans), metakaolin reacts with the calcium hydroxide (lime) byproducts produced during cement hydration.(Fig.3.3)

Fig 3.3 Metakaolin

Fig3.4 Selfconsolidating concrete using metakaolin

3.3 PULVERISED FUEL ASH (PFA)

The Lands and Works Branch Practice Note on Concrete Technology No. 4, The Use of Pulverised Fuel Ash in Structural Concrete, was issued in 1983. It was stated therein that the Note would be reviewed when more information on the local use of PFA was available. There is more information available now, but there is nothing which requires the Note to be amended. There are, however, other factors which make the issue of this Addendum desirable.(Fig.3.4)

IV. Result and Discussion

Fig 4.1 comparison of the effect of CSF and MK on the dosage of air entraining agent to obtain 7±1 % air content in the fresh concrete

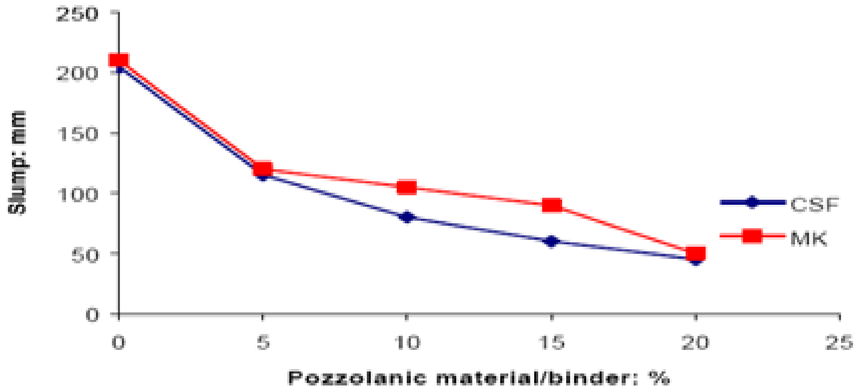


Figure 2 Comparison of the effect of CSF and MK on the slumps obtained for concretes shown in Figure 1

Fig 4.1 indicates comparison of the effect of CSF and MK on the dosage of air entraining agent needed to attain 7.5 0.6 % air content of the fresh mix is shown in Figure 1. A constant amount of superplastisizer of 0.35% by mass of the binder was adopted for both CSF and MK mixes. The dosage of air entraining admixture required to produce a given volume of air in concrete containing more than 5% CSF or MK, as partial mass replacement for PC, increases markedly with increasing amounts of CSF or MK. The admixture requirement rises very sharply for increase in CSF or MK content from 15 to 20%, indicating even higher air entraining admixture demand for higher amounts of the two pozzolanic materials. The trend of this increase is identical for both CSF and MK concretes. However the CSF concrete is more demanding in air entraining agent than MK concrete. This is primarily due to the higher specific surface of CSF which leads to more air entraining agent being adsorbed and fewer molecules of the agent available to be adsorbed at the air-water interfaces. The carbon content of CSF (Table 1) will also contribute to this additional adsorption. The measured slumps for these mixtures were in the ranges 45-210 mm and 50-210 mm for the CSF and MK concretes respectively. Figure 2 shows the variations in the slump with the level of pozzolanic replacements. The results demonstrate the higher water demand of CSF as compared to MK, as the replacement level increases. The inconsistency in the results obtained for the 20% replacements is attributed to specimen variability.

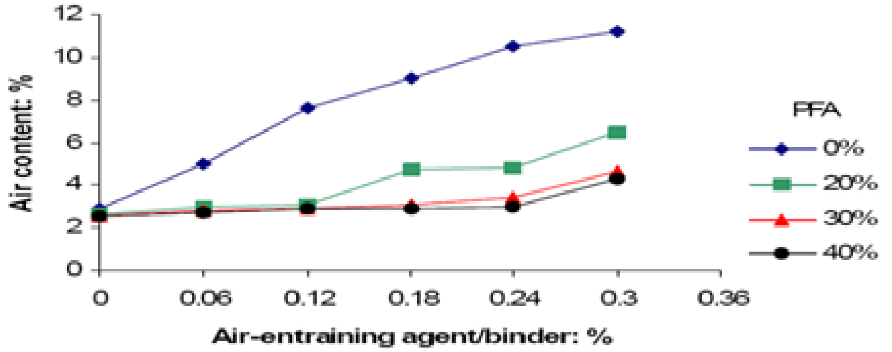


Figure 6 Effect of air entraining agent on air content of control and PFA concrete with 0.3% of superplasticizer

Fig 4.2 comparison of the effect of CSF and MF on the slumps obtained for concretes

Figure 4.2 indicates a constant dosage of air entraining agent (0.06%) and the target air content was achieved even at the higher cement replacement levels. This suggests that the presence of super plasticizer enhances the ability of the air entraining agent to entrain air in concrete containing these two pozzolanic materials possibly by competing with the latter for surface adsorption sites.

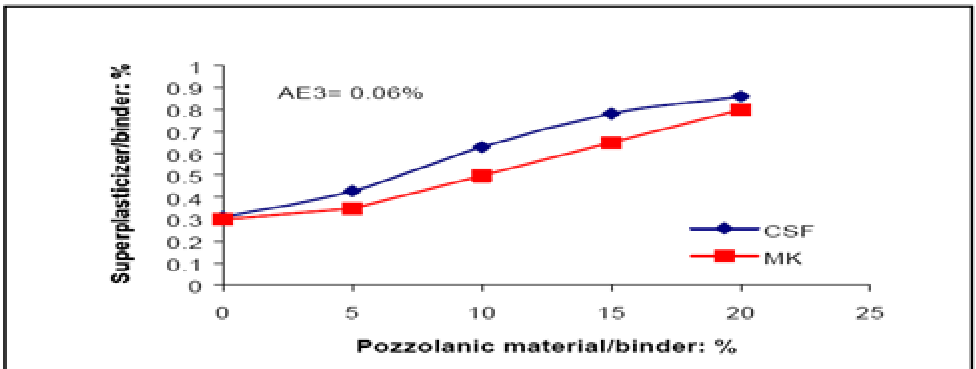


Figure 3 Comparison of the effect of CSF and MK on the dosage of superplasticizer required to obtain 6±1 % air content and 100±20 mm slump in the fresh concrete

Fig 4.3 comparison of the effect of CSF and MK on the dosage of super plasticizer required to obtain 6 ±1 % air content and 100±20 mm slump in the fresh concrete

Figure 4.3 gives the variations in the measured air contents in the control and CSF concrete with increasing dosage of air entraining agent. The results clearly demonstrate the efficiency of the admixture in entraining air in all the concretes investigated. It is seen that sharp rises in the air contents are obtained for dosages up to 0.12%. Dosages greater than 0.12% have less influence on air content in the case of 20% CSF whereas the air content of the control and 10% CSF concretes show continuous increase. A similar behavior was encountered by Carette and Malhotra who found it difficult to entrain more than 6% air in concretes with 20% CSF.

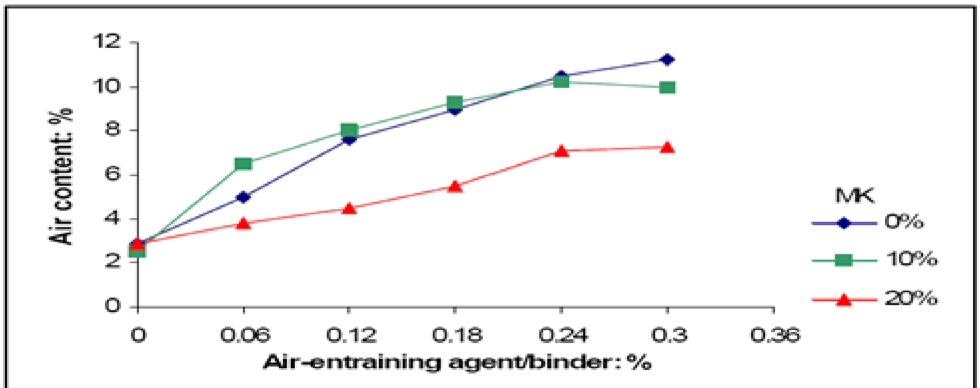


Figure 5 Effect of air entraining agent on air content of control and MK concrete with 0.3 and 0.5 % superplasticizer respectively

Fig 4.4 Effect of air entraining agent on air content of control and MK concrete with 0.3 and 0.5% super plasticizer respectively

Figure 4.4 gives the variations in the measured air contents of MK concrete with increasing air entraining agent. Again as with CSF concrete, the results show the efficiency of the admixture in entraining air in such concretes. It is seen that steady increases in the air contents are obtained for dosages up to 0.24%. This optimum limit is significantly greater than the limit of 0.12% dosage exhibited by CSF concrete.

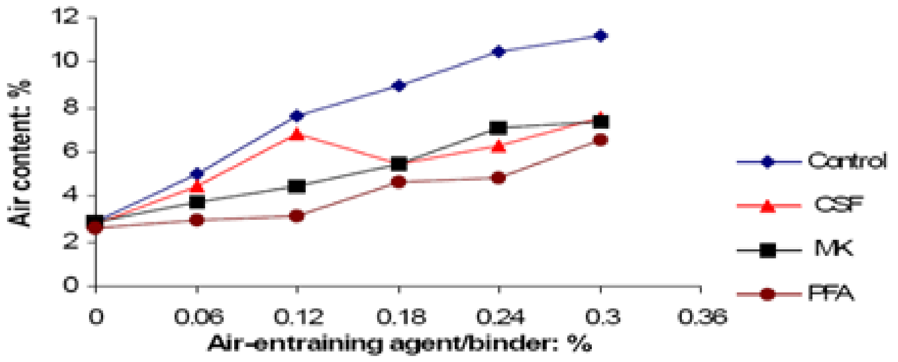


Figure 7 Comparison of the effect of air entraining agent on air content of control and 20% CSF, MK and PFA concrete

Fig 4.5 Effect of air entraining agent on air content of control and PFA concrete

Fig 4.5 also indicate that it would be difficult to entrain air in excess of about 6%, (though normally not desirable) in 20% MK concrete even with high dosages of air entraining agent. In the case of 10% MK, air contents in excess of 10% may be entrained. Similar results were encountered in the case of the CSF concretes. This behaviour is attributed to the dispersal effects when high dosages of air entraining agent are used in conjunction with high pozzolan levels, leading to greater adsorption rates
entraining agent on air content of control and PFA

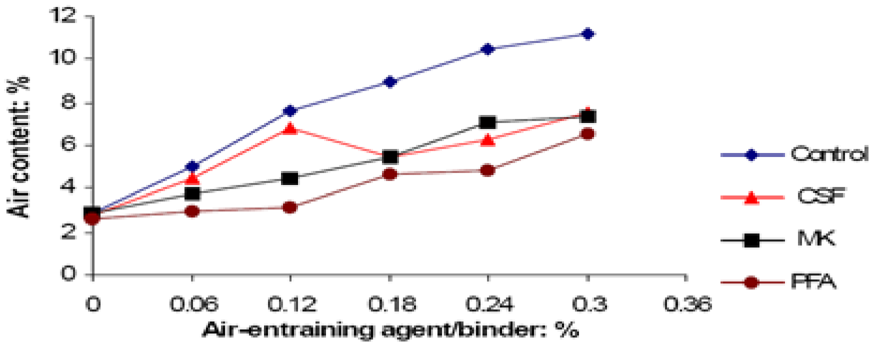


Figure 7 Comparison of the effect of air entraining agent on air content of control and 20% CSF, MK and PFA concrete

Fig 4.6 comparison of the effect of air entraining agent on air content of control and 20% CSF, MK and PFA concrete

Figure 4.6 shows the large the air content caused by the incorporation of PFA, irrespective of the dosage of the air entraining agent. This reduction increases as the PFA level increases for all dosages of the admixture. Although moderate increases in air content are obtained for the 20% PFA concrete, albeit at the cost of high dosages of the

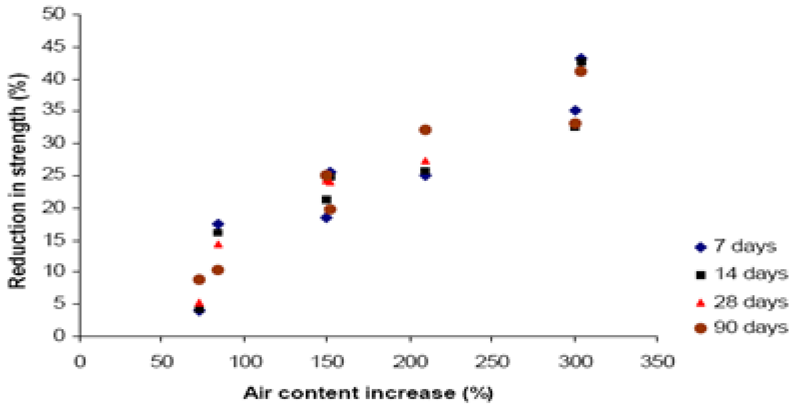


Figure 8 Percentage strength reduction versus percentage air content increase for ncretes under investigation at different curing ages

Fig 4.7 percentage strength reduction versus percentage air content increase for concretes under investigation at different curing ages

Figure4.7 gives a plot of the percentage reductions in strength with percentage increases in the air content of concretes incorporating CSF, MK or PFA. It can be seen that the relationship between the percentage reductions in strength and the percentage increases in strength is almost linear with the exception of those reductions corresponding to small increases in the air content of the fresh concrete.

Table 4.1 summarises the results for the compressive strength reductions at each of the ages of 7, 14, 28 and 90 days corresponding to increases in the air contents for concretes incorporating CSF, MK or PFA & Effect of increase in air content on reduction in compressive strength.

Table 4.1 Results for the compressive strength reductions

Concrete	Air Content Increase (%)	Reduction in strength(%)			
		7 days	14 days	28 days	90 days
Control	210	25	26	27	32
10% CSF	304	43	43	41	41
10% MK	300	35	33	33	33
20% MK	152	25	25	24	20
20% PFA	150	18	21	24	25
30% PFA	84	18	16	14	10
40% PFA	72	4	4	5	9

For example when the air content in 10% CSF concrete increases by 304% i.e. from 2.6 to 10.5% there is a reduction in the 28-day compressive strength of 41%. The reduction in the 28-day strength of the 10% MK concrete corresponding to an increase in the air content of 300%, i.e. from 2.5 to 10% is 33%. Similar effects are produced in the PFA concretes. For example an increase in air content of 150%, i.e. from 2.6 to 6.5% in 20% PFA concrete gives a reduction in the 28 day strength of 24%. The results show that irrespective of the curing time, the percentage reductions in strength due the increase in air content are more or less the same for all concretes considered in the present study.

V. Conclusions

The following conclusions may be drawn from the work reported in this paper:

For a given slump and air content CSF has more demand for superplasticiser and air entraining admixtures than MK. The superplasticiser enhances the performance of the air entraining admixture and/or itself plays a secondary role in entraining air to the fresh concrete. A three fold increase in slump is produced in control and 10% CSF concretes by adding 0.12% of air entraining admixture.

Although further additions of the admixture lead to increased slump in the control, little benefit in workability is exhibited by the CSF concrete. This is attributed to the greater diffusion of the air entrain inggent and consequent adsorption of the admixture by the very fine CSF particles. Up to 0.12% air entraining admixture results in steep rises in the air content of superplasticised CSF concrete.

The benefits of higher levels of the admixture diminish, particularly in the concretes with high CSF contents (20%). The superplasticiser plays an important role in increasing the air content of low level CSF concrete. Up to 0.24% air entraining admixture results in a steady increase in the air content of MK concrete. This is compared to a limit of 0.12% for CSF concrete. Non-air entrained control, CSF and MK concretes all have the same volume of naturally entrapped air (approximately 2%).

This is attributed to the role played by the additional superplasticiser used in the CSF and MK concretes. PFA causes large reductions in the air content of fresh concrete, irrespective of the dosage of the air entraining admixture. The compressive strength of all concretes show systematic and more or less linear reductions with increasing air contents (2 to 10%) of the fresh concrete. Further analysis is done with software for extra accuracy in result.

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