Effect of binder chemistry on sulphate resistance of fly-ash blended cement concrete mixes

M Nazeer¹, M C Narasimhan² and S V Rajeeva³

¹Professor, Dept. of Civil Engineering, TKM College of Engineering, Kollam – 691005, India.
²Professor, Dept. of Civil Engineering, NITK Surathkal, India.
³Former Professor, Dept. of Civil Engineering, NITK Surathkal, India.

Abstract. The chemical durability of concretes exposed to sulphate environment largely depends on the quality and quantity of products of cement hydration. Certain hydration products are readily reactive with the sulphate ions and form expansive products such as gypsum and ettringite. On the other hand, some sulphate compounds participate in reducing the cementing property of hydration products. These reactions cause expansion and deterioration of strength of concrete. Sulphate resistance of concrete can be improved by the incorporation of Supplementary Cementitious Materials (SCMs). Reduced water-binder ratio and proper curing can make concrete more durable in sulphate environment. This paper reports the details and results of an investigation of effect of chemical composition of binder materials on the sulphate resisting property of concrete exposed to a rich MgSO₄ solution. The effect of initial curing is also investigated so that it may be possible to suggest the mix compositions for typical field applications of concrete. The variables investigated in this report are the oxide composition of binder components and the initial curing conditions. A set of concrete mixes, all with a constant binder content and water-binder ratio are used in the investigation.

1. Introduction

Concrete is, as at present, the most widely used construction material. The superiority of concrete amongst the construction materials is due to number of advantages presented by its use which include ease in mouldability to any required size and shape, water resistance, lower cost and less energy input required for its manufacture. Concrete technology, an experimental science, is in a period of rapid development. Research activities are in full swing to try alternate materials which can replace the conventional concrete ingredients.

All the basic ingredients of conventional concrete are of geological origin. Over-exploitation of these materials from the nature causes serious ecological imbalances. Again, increased manufacturing of cement, which emits carbon dioxide (a green-house gas, at the rate of one ton of CO₂ for every ton of cement) is also blamed for its share in global warming and related problems. Natural sand and aggregate supplies are being exhausted in many areas of the world, focusing more attention on manufactured sand and recycled aggregates.

These factors strongly demand active research in the area of cement and concrete technology, especially on new materials to replace the conventional concrete ingredients. Use of cement can be minimized by replacing it (partially) with supplementary cementitious materials. Most of the supplementary cementitious materials used are industrial waste materials such as fly ash, ground
granulated blast furnace slag, silica fume and rice-husk ash. The use of industrial by-products as supplementary cementitious materials has two advantages:

- It offers solution for the problem of safe and economic disposal of industrial wastes.
- The use of these materials improves the micro-structure of concrete improving its structural and functional performance and would lead to reduced cement consumption.

The service life of the structure depends on the durability of the materials used for the construction. A material is assumed to reach the end of its service life when its properties under given condition of use has deteriorated to an extent that the continuing use of the material is ruled either unsafe or uneconomical [1]. In the design of concrete structures, durability must become the first and foremost concern because, if the material of concrete used in it does not survive for the required period, or if it is not displaying the desired properties, the structure is neither safe nor economical. The most expensive concrete is the one which has to be replaced [2].

Concrete using ordinary Portland cement is most vulnerable to sulphate attack. In comparison, concretes made of sulphate resisting Portland cement, Portland pozzolana cement or Portland blast-furnace slag cement have greater resistance to sulphate attack. But they are not immune to such attack at all situations and at all concentrations of sulphate solution. The action of sulphates and the protection of concrete against their damaging effects are therefore matters of great concern, which require extensive investigation [3]. According to DePuy [4], the results from laboratory studies of sulphate attack are insufficient to completely understand the chemistry behind it. However, results from such studies essentially reveal the sulphate resistance potential of tailor-made concrete mixes.

Concretes exposed to ground water, sulphate bearing soils and marine environment are susceptible to sulphate attack. Among the various sulphate salts present in these sources, magnesium sulphate is more harmful to concrete. The two best-recognised chemical consequences of sulphate attack on concrete components are the formation of ettringite and gypsum. The formation of ettringite can result in an increase in solid volume leading to expansion and cracking. On the other hand, the formation of gypsum can lead to softening and loss of concrete strength [5]. A large volume of literature is available in the area of sulphate attack on concrete [6-10].

The rapid increase in the use of fly ash as a supplementary cementing material is due to the economical and environmental considerations. Fly ash is a by-product of the coal-based power generation and consists mainly of SiO₂, Al₂O₃, Fe₂O₃ and CaO and some impurities. A large volume of literature is available in the area of application of fly ash in concrete [11]. Many of the laboratory level experimental works on sulphate resistance is performed on binder pastes (with or without admixing fly ash) or mortar specimens [12-15]. The results from these investigations may not be directly applicable to concrete, because of the resistance of coarse aggregates to expansion of concrete.

2. Research significance
Chemical durability of concrete depends on the relative quantities of hydration products which further depend on the composition of cementitious materials used in concrete. The extent of curing also affects the rate of development hydration products and micro-structure of concrete. Limited research has been reported on the effect of oxide composition of total binder material on the sulphate resistance of concretes incorporating supplementary cementitious materials. This investigation aims to address the effects of potential oxides on the strength deterioration of concrete mixes containing fly ash as partial replacement to ordinary Portland cement.

3. Experimental investigation
The present investigation is aimed to study the effect of the dosage of fly ash on the sulphate induced durability issues of concrete mixes. Fly ash is used as a cement replacement (partial) material. Four different replacement levels are investigated in this study (15%, 25%, 35% and 40%). The concrete mix with cement alone as the binder is considered as the control mix. For each mix, four different exposure conditions (Types) are investigated as detailed below with their practical significance:

- Type I: specimens exposed to sulphate solution immediately after 24 hours of casting, as cast-in-situ concrete piles exposed to sulphate environment,
Type II: specimens exposed to sulphate solution after initial moist curing for 7-days, as structural elements exposed to sulphate environment after minimum period of moist curing, like concrete in column footings,

Type III: specimens exposed to sulphate solution after initial moist curing for 14-days, as where concrete structural elements can be sufficiently moist cured, like pre-cast construction works, and

Type IV: Specimens continuously cured in tap water up to test, for comparison purposes.

The sulphate solution (exposure medium) is prepared in the laboratory by dissolving 25.66g of MgSO₄.7H₂O in water for one litre solution. This dosage corresponds to a sulphate ion concentration (in solution) of approximately 10000 ppm. To evaluate the performance of fly ash admixed concrete in sulphate environment, 100mm cubes are tested for their strengths at different ages extending up to 2 years (720 days) of casting.

3.1. Materials

The concrete mix used for the investigation is designed for a characteristic compressive strength of 70 MPa (10000 psi). The cement used in the preparation of such mix should possess better strength and rheological properties. As the objective of the study is to evaluate the durability enhancement of concrete mixes with fly ash admixed as a supplementary cementitious material, it is decided to use ordinary Portland cement. Also, to get the maximum advantage on initial strength development of concrete and reduced consumption of cement, ordinary 53-Grade Portland cement [16] has been used. Physical tests are carried out according to the National standards [17] to evaluate the acceptability of cement. The chemical composition of cement is analysed using a Scanning Electron Microscope (SEM).

Fly ash used in the present investigation was procured from a state-owned thermal power station. Physical tests are carried out according to the National standards [18]. The comparison of results of chemical analysis on this fly ash with the National standards [19] shows that the material is siliceous based. As per ASTM classification [20], it is a low-calcium, Class-F fly ash. The physical properties of the cement and fly ash are listed in Table 1.

The oxide (%) composition of cement and fly ash are presented in Table 2. Locally available crushed granite aggregate is used as coarse aggregate. The coarse aggregate used for the preparation of concrete mixes is made by blending two fractions, namely, CA-I, with size varying from 10 mm to 20 mm, and CA-II, with particles having sizes between 6 mm to 10 mm, in the ratio 3:2, so as to get all-in graded aggregate. Locally available river sand is used as fine aggregate in the present investigation. The details of the physical properties of the aggregates used in the investigation are presented in Table 3.

**Table 1. Physical properties of cement and fly ash**

| Parameter                        | Cement | Fly ash |
|----------------------------------|--------|---------|
| Physical Characteristics         |        |         |
| Specific gravity                 | 3.16   | 2.18    |
| Standard consistency, %          | 30     | --      |
| Blaine’s fineness, m²/kg         | 385    | 410     |
| Initial setting time, Minutes    | 95     | --      |
| Final setting time, Minutes      | 270    | --      |
| Compressive strength, MPa, at    |        |         |
| 3 days                           | 32     | --      |
| 7 days                           | 45     | --      |
| 28 days                          | 58     | --      |
Table 2. Oxide composition of cement and fly ash

|       | CaO  | SiO₂  | Al₂O₃ | Fe₂O₃ | SO₃  | MgO  | Mn₂O₃ | P₂O₅ | TiO₂ | K₂O  | Na₂O | Na₂Oeq | LoI |
|-------|------|-------|-------|-------|------|------|-------|------|------|------|------|--------|-----|
| Cement | 64.78| 19.11 | 4.04  | 6.35  | 4.55 | 0.64 | 0.13  | 0.25 | 0.18 | 0.6  | --   | 0.39   | 1.36|
| Fly ash| 1.79 | 58.87 | 32.17 | 2.93  | 0.49 | 0.92 | --    | 0.56 | 0.76 | 1.14 | 0.37 | 1.12   | 2.54|

Table 3. Physical properties of aggregates

| Properties       | Fine aggregate | Coarse aggregate |
|------------------|----------------|------------------|
| Fineness modulus | 2.17           | 6.65             |
| Specific gravity | 2.6            | 2.67             |
| Water absorption, % | 1.8           | 0.91             |

A commercially available high-range water-reducing admixture is used for enhancing the workability of concrete. The marsh cone method is used to determine the optimum dosage of this superplasticiser. The saturation point, which corresponds to the dosage of superplasticiser, beyond which any increase in its quantity has no appreciable effect on rheology of the cement grout, is found to be 2.25% by mass of cement.

3.2. Mix proportions and mixing

Concrete mix is designed for a characteristic compressive strength of 70 MPa (10000 psi). The method adopted for the design is similar to the one recommended by [21]. The design basically involves the determination of water-binder ratio for the required compressive strength. Selecting suitable water content, depending on the slump requirement and maximum size of aggregate, the cement requirement is determined. The coarse aggregate content is determined depending on the shape of the aggregate. The fine aggregate content is then calculated from absolute volume basis with volume of entrapped air assumed as 2% [22]. The mix proportions obtained based on the above procedure are finalised after minor adjustments on the quantities of constituent materials. For the complete investigations, a reference concrete mix of proportions 1: 1.55: 2.17 with a w/b ratio of 0.30 and cement content (only binder) at 483 kg/m³ is adopted.

As mentioned earlier, four different replacement levels of cement with fly ash are considered in this investigation. The lower limit (15%) corresponds to low blending [23]. The upper limit (40%) is fixed in such a way that the resulting blend does not fall in the domain of high-volume fly ash concrete. For the specified cement content of the reference mix and the relative specific gravity values of materials used in this investigation, 40% replacement (by mass) of cement with fly ash is about 50% (by volume) of the total binder. The details of mix proportions adopted in this investigation are presented in Table 4.

Table 4. Details of concrete mix proportions, kg/m³

| Mix Designation | Cement | Fly Ash | Fine aggregate | Coarse aggregate | Water | Superplasticizer |
|-----------------|--------|---------|----------------|------------------|-------|-----------------|
| Control         | 483    | --      | 747.3          |                  |       |                 |
| FA15            | 410.5  | 72.5    | 725            |                  |       |                 |
| FA25            | 362.3  | 120.7   | 707            | 1050             | 145   | 10.87           |
| FA35            | 314    | 169     | 690            |                  |       |                 |
| FA40            | 289.8  | 193.2   | 681            |                  |       |                 |

A horizontal shaft mixer is used for the preparation of concrete, following a mixing sequence as outlined below for all mixes:
The mixer is initially loaded with coarse aggregate and run for 30 seconds pouring sufficient water to wet the surface of aggregate.

Fine aggregate is introduced to the mixer and mixing continued till the partially wet mix looks homogeneous.

The binder (mixture of cement and fly ash) is then introduced and about three-quarter of the water, premixed with the required quantity of super-plasticizer is poured-in gradually.

The mixing is continued for a period not less than four minutes. The balance of water-super-plasticizer mixture is added at the end of this period and the mixing is continued for a further period of not less than one minute.

The mix is poured out and used for casting the specimens.

3.3. Testing
Concrete cubes are tested for their compressive strength at different ages of (3 - 720 days) of curing. A 2000 kN-capacity, analog-type compression testing machine is used for this purpose. The specimens taken out of the curing media are wiped to remove excess surface water, weighed and tested as per the National standards[24]. Care is taken to check the calibration of the compression testing machine at regular intervals. The variations on the observed values for a particular set of observations are well within the permissible limits (less than 5% in most of the cases).

4. Results and discussion

4.1. Oxide composition
The percentages of major oxides in the total binder for different PC-FA blends are presented in Table 5.

|        | Control | FA15 | FA25 | FA35 | FA40 |
|--------|---------|------|------|------|------|
| CaO    | 64.78   | 55.33| 49.03| 42.73| 39.58|
| SiO₂   | 19.11   | 25.07| 29.05| 33.03| 35.01|
| Al₂O₃  | 4.04    | 8.26 | 11.07| 13.89| 15.29|
| Fe₂O₃  | 6.35    | 5.84 | 5.50 | 5.15 | 4.98 |

It may be observed that, an increase in the partial replacement of cement by fly ash causes a corresponding reduction in the CaO and Fe₂O₃ contents in the total binder but an increase in the SiO₂ and Al₂O₃ contents. A good part of CaO is also required for hydration of cement to C-S-H but hydration reactions themselves will also yield Ca(OH)₂. As CaO is the source of Ca(OH)₂ after hydration, the reduction in CaO may show an improvement in the properties of hardened concrete. As SiO₂ is responsible for the pozzolanic reaction and the formation of secondary calcium-silicate-hydrate, the increase in SiO₂ may cause improvements in the properties of hardened concrete. The higher alumina content and reduced Fe₂O₃ content may enhance the vulnerability of concrete to sulphate attack. However, such effects of SiO₂, Al₂O₃ and Fe₂O₃ on chemical durability of PC-FA blends would also depend on the reaction potential of these oxides in the particular blend.

4.2. Compressive strength
The development of compressive strength of the control mix, exposed to different curing conditions, with time is illustrated in Figure 1. In all exposure conditions, the maximum strength is reached at the age of 90 days. The reduction in strength of mixes in Type II, Type III and Type IV curing during the period between 90 to 360 days indicate the leaching of Ca(OH)₂ produced during early age hydration. Similarly the increase in strength at later ages (beyond 360 days) for Type III and Type IV curing...
indicate the delayed hydration of cement in the mix, as there may be a good part of higher cement content of this mix with a lower w/c ratio left unhydrated at early ages, getting into hydration reaction with an inordinate delay. This control concrete mix does not show any increase in strength after 360 days in Type II curing. The exposure of the reference mix to sulphate environments at early ages (Type I and Type II exposure) causes strength deterioration. The early exposure to sulphate environment (MgSO$_4$ solution) causes the formation of brucite [Mg(OH)$_2$] which inhibits the further hydration of un-hydrated cement in the mix. In Type I exposure the sulphate deterioration starts at the age of 180 days.

The development of compressive strength of the various PC-FA blends in different exposure conditions are presented in Figure 2. As observed in the case of control mix (Figure 1), there is a reduction in compressive strength of all PC-FA mixes in Type IV curing after 90 days. While this reduction is not significant in blends with lower replacement levels (FA15 and FA25), significant reduction in compressive strength is observed for FA35 mix after 180 days, whereas in FA40 mix the strength reduction is observed between 90 and 180 days. The improvement in compressive strength after the above reductions is significant for blends with higher fly ash contents. This clearly indicates that the pozzolanic activity of fly ash in concrete is more in blends containing higher percentage of fly ash. These results are in agreement with the findings of Wang et al. [25]. In the present investigation, it is observed that the increase in compressive strength between 360 to 720 days, in control curing, for F15, FA25, FA35 and FA40 are respectively 5%, 1%, 6% and 8%.

![Figure 1. Strength development of control mix in different exposure conditions](image)

As shown in Figure 2(a), FA15 mix undergoes significant sulphate attack in Type I and Type II exposure conditions. The strength deterioration begins at the age of 180 days and continues with a constant rate. A prolonged initial moist curing (Type III) enhances the sulphate resistance of this mix. This behaviour is due to the formation of brucite resulting from an early exposure to sulphate environment prevents the later-age hydration and the pozzolanic action. Prolonged moist curing provides a favourable condition for the completion of the hydration and the associated pozzolanic reaction. For FA25 mix, in Figure 2(b), strength deterioration occurs for all types of sulphate exposure. Deterioration begins at an early age of 180 days in Type I exposure and after almost 360 days for other exposure types. For FA35 mix (Figure 2(c)), no significant strength deterioration was observed in any of the exposure conditions. However, prolonged moist curing before sulphate exposure increases the sulphate deterioration risk of PC-FA blends with higher replacement levels (FA35 and FA40). But these mixes are more stable in Type I exposure.
To determine the effect of curing, the percentage loss in compressive strength of a mix at a specified age is determined by deducting the strength of the specimen cured/exposed in a particular environment from the strength of same mix cured in water and expressed as a percentage of strength of specimen cured in water. Negative values of strength loss indicate a gain in compressive strength in the exposure medium. The strength deterioration Vs age curves of PC-FA blends (Figure 3) indicate that, irrespective of the cement replacement level and the extent of initial moist curing, all PC-FA blends undergo strength deterioration in sulphate environment. From the results, it may be also be concluded that FA40 mix can perform better in situations where concrete is exposed to sulphate environment without any initial moist curing. While even with moderate initial moist curing up to 7 days, FA35 mix is exhibiting smaller strength-losses due to sulphate deterioration, FA15 mix would be able to reasonably resist sulphate attack only after prolonged initial moist curing (14 days).

The contents of oxides CaO, Al₂O₃ and Fe₂O₃ present in the total binder are now used in the calculation of an oxide factor, also named as resistance factor, \( R_x \), as:

\[
R_x = \frac{\text{strength of specimen cured in a particular environment}}{\text{strength of specimen cured in water}}
\]
This ratio is selected based on the trend of sulphate deterioration with individual oxide composition. Dunsten [26], reported the effect of resistance factor, $R$, based on the CaO and Fe$_2$O$_3$ contents in the fly ash alone, on the sulphate resistance of fly ash blended concretes. In the present investigation, there seems to exist a relation between $R_f$ of the binder in PC-FA blends, as defined above and the loss in compressive strength at 720 days of continuous exposure to sulphate environment (Type I) [Figure 4]. The relation can be written as follows:

$$Loss(\%) = 8.28R_f - 1.39$$

Figure 4. Variation of compressive strength loss against oxide composition of PC-FA blends at 720 days in type I exposure

5. Conclusions

On the basis of experimental results reported herein, the following specific conclusions are drawn within the range of parameters investigated.

- The pozzolanic activity at higher percentage replacement of cement with fly ash (>25%) in PC-FA blends enhances the sulphate resistance of mix in Type I exposure. For lower replacement levels (<25%) prolonged initial moist curing improves the sulphate resistance.
- The early exposure of control mix to sulphate environment causes the formation of relatively impermeable brucite which inhibits the further hydration of unhydrated cement in the mix.
- The mechanical strength deterioration of PC-FA blends exposed to sulphate environment can be correlated with the oxide composition of total binder used in the system.

In the light of these observations, it may be possible to suggest suitable binary compositions of PC-FA blends to satisfy the requirements of concrete for a particular application in the field.

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