# A Review On Effect Of Admixtures On Durability Properties Of Concrete

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#### **Abstract**

The effects of admixtures on mechanical properties is well known and hence are used in industry for enhancing the same. However using admixtures to improve durability is not conventional. Therefore study of effect of admixtures on durability property is significant. In this paper a review study on effect of Fly Ash, Silica Fume, Zeolite and Metakaolin on water absorption, sulphate attack, chloride ion penetration, Sorptivity, carbonation, alkali silica reaction and freeze thaw cycle has been done.

Keywords: Admixtures, Fly Ash, Silica Fume, Zeolite, Metakaolin, Water absorption, Sulphate attack, Chloride ion penetration, Sorptivity, Carbonation, Alkali silica reaction and Freeze thaw cycle

#### Introduction

The ability of concrete to withstand the conditions for which it is designed without deterioration for a long period of years is known as durability. In other words, durability is defined as the capability of concrete to resist weathering action, chemical attack and abrasion while maintaining its desired engineering properties. It normally refers to the duration or life span of trouble free performance. The main factors which adversely affect durability are, Freezing and thawing action, Percolation / Permeability of water, Temperature stresses i.e. high heat of hydration, Alkali Aggregate Reaction, Sulphate Attack, Chloride Ingress, Delay Ettringite Formation, Corrosion of reinforcement etc.

In present scenario, concrete is being used for various purposes in vivid conditions. Therefore, ordinary concrete may fail to exhibit the required strength and durability in such conditions. In such cases, admixture is used to modify the properties of concrete so as to make it more suitable for any such situations. Admixtures are used as ingredients of concrete and added to the batch immediately before or during mixing. Keeping global sustainable development in mind, it is necessary that supplementary cementing materials should be used to replace large proportions of cement in the construction industry and must be cost effective as well.

# Requirement of durability study

Durability is the capability of maintaining the serviceability of a structure over a specified time, or a characteristic of the structure to function for a certain time with required safety and corresponding characteristics, which provide serviceability. Structures contain elements that can last more than 100 years such as foundations, walls and floor slabs, while on the other hand there are components that need frequent replacing. The durability of a structure is its resistance against the actions from the environment surrounding the structure. However, some structures, depending on their quality and environmental aggressiveness, have not satisfactory durability.

The generally accepted aim of a design is to achieve an acceptable probability that the structure being designed will perform satisfactory during its intended life. In order to construct a durable and a reliable concrete structure, it is necessary to design it for durability and provide required service life. Service life is the period of time after construction during which all properties exceed the minimum acceptable values when routinely maintained. Serviceability is viewed as the capacity of the structures to perform the functions for which they are designed and constructed within normal use conditions. The terms lifetime and working life are also used in literature. The European standard for structural safety EN 1990 prescribes 50 years for buildings and 100 years for monumental building structures, bridges and other civil engineering structures. A service life design conditions the designer's choice of fundamental properties to fulfil all functional requirements during the target time. Defects in materials may lead to week serviceability of a structure.

The key step is defining a target service life. In practice there are three different types of service life depending on the type of considered performance: Technical service life is the time of service until acceptable state is reached (failure). Functional service life is the expected time in service until the structure no longer fulfils the functional requirements. Economic service life is the time in service until the replacement of the structure is economically justified more than keeping it in service. Mostly the service life problem is mainly technical type, with the sub-aspects like mechanical and other structural performances, serviceability, and aesthetics. Real service life must not be shorter than nominal life. The two phases of deterioration which are considered while defining target service life are:

- The initial phase (period) in which there is no noticeable weakening of properties, except a protective barrier (the duration of this phase is about 15 years). Corrosion is initiated by chlorides or carbonation.
- The propagation phase with active deterioration mechanisms that develop increasingly with time. The propagation period consists of the propagation with

minor damage and the accelerated period (the duration of this phase is about 15 years). After that follow the accelerated period with widespread cracking and spalling of the protective layer (cover).

# Effect of admixtures on durability of concrete

Admixtures are those ingredients in concrete other than portland cement, water, and aggregates that are added to the mixture immediately before or during mixing. Two main types of admixtures are, namely chemical admixtures and mineral admixtures. Chemical admixtures include Accelerators, Retarders, Water-reducing agents, Super plasticizers, Air entraining agents etc. and mineral admixtures include, Fly-ash, Blast-furnace slag, Silica fume, Rice husk Ash etc.. Various durability properties are discussed below.

# A. Water absorption

Durability of concrete is mainly dependent on the capacity of a fluid to penetrate the concrete's microstructure, which was called permeability. High permeability led to the introduction of molecules that react and destroy its chemical stability. Moreover, low permeability of concrete can improve resistance to the penetration of water, sulphate ions, chloride ions, alkali ions, and other harmful substances which caused chemical attack. Concrete permeability had a close relationship with the characteristics of its pore structure in the cement paste and the intensity of micro cracks at the aggregate-cement paste interface as well as within the paste itself. Here, pore structure mainly involved volume and size of the interconnected capillary pores. As we know, the hydration reaction of cement results in a product consisting of solid and pore systems. The pore network of a cement paste matrix provides passage for the transport of fluid into concrete and its development depends on a number of factors including the properties and composition of the concrete constituent materials, the initial curing condition and its duration, the age at testing, and the climatic exposure during drying and conditioning of the concrete. The temperature of curing and the duration of moist curing are also key factors for proper pore structure. The effectiveness of initial curing becomes more important when mineral admixtures like fly ash are used as partial substitution for cement in concrete. Numerous workers have reported that mineral admixtures require a relatively long curing period for the favourable pozzolanic effect on the performance of concrete to be realized. A common procedure to assess water absorption is discussed below.

Water Absorption test is done after 28 days of curing. The specimens are then taken out from the curing tank and dried for 24 hours. The dried specimens are weighed accurately and noted as dry weight. The dried specimens are then immersed in water. Weight of the specimens at pre-determined intervals are to be taken after wiping the surface with dry cloth. This process should be continued for not less than 48 hours or up to constant weight is obtained in two successive observations.

Previous studies shows that Zeolite has higher water permeation than Silica Fume or Metakaolin due to its permeability factor. The 24 h of water absorption is highly dependent on the amount of capillary pores and plays a more important role in water permeation, causing the specimens containing SF and Metakaolin to permeate less water. Also, 24 h of water permeation is highly affected by the amount of pozzolan used in concrete. In case of half-hour permeations specimens containing SF with different levels of substitution show less variation than the other two pozzolans. This indicates that SF is influenced more by the curing condition than the other two pozzolans which leads to micro cracks on the surface of the concrete and thereby increases water permeation in specimens with SF when compared to other pozzolans with same water-to-cement ratio of 0.35. Further use of zeolite has a greater influence on half-hour permeations due to its higher permeability factor. The use of zeolite at 20% slightly increased the water absorption and porosity, which is undesirable, but increasing this percentage even more caused a slight reduction in water absorption. On the other hand, increasing the replacement percentages of SF and Metakaolin causes a small decline in water absorption and porosity.

Another study showed that saturated water absorption and porosity of HPC mixes containing silica fume, metakaolin and fly ash were lower when compared with that of the concrete mixes without admixtures. Cement replacement level of 15 percent with all the three admixtures in concrete mixes was found to be the optimum level to obtain lower value of the saturated water absorption and porosity at the age of 28 days. The results of saturated water absorption and porosity tests have demonstrated superior durability characteristics of HPC mixes containing admixtures. This is due to the fact that micro structure in cement paste matrix is improved due to pozzolanic action and micro-pore filler effects of silica fume, resulting fine and discontinuous pore structure. Even a partial replacement of cement with admixtures in concrete mixes leads to considerable savings in consumption of cement and gainful utilization of mineral admixtures.

Further studies proved that blended concrete showed better resistance against water absorption than any other. Out of the various admixtures used combination of Fly Ash 20% + Rice Husk Ash 10 % and Fly Ash 20 % + Silica Fume 10 % showed the best result compared to M30 concrete whereas the combination of rice husk ash and silica fume shows lower result than the control concrete due to inherent chemical reactions.

#### B. Sulphate attack

Sulphate attack occurs when calcium hydroxide and aluminates in the cement reacts with the sulphates contained in soil and seawater. The presence of a large quantity of chlorides in seawater inhibits the expansion experienced by concrete where groundwater sulphates have constituted the attack. Deterioration of concrete in environments containing chloride has led to the development of concrete resistant against sulphate attack by the addition of admixtures. Two basic forms of sulphate attack are as follows:

- Reaction between aluminates and gypsum in cement
- Acid interaction of sulphate ions and calcium hydroxide (causing gypsum formation).

If the quantity of reactive aluminates in the cement is too high, then excessive reactive aluminates in hydrated form will be available to react with sulphates after hardening of cement. This is harmful, as it will produce expansive ettringite and cracking of the concrete. This process has been summarized as:

Aluminate Hydrate + Ca(OH)2 + sulphate + H2O ==>Ettringite

The second principle of gypsum formation has been shown below:

Ca(OH)2 + sulphate + water ==> Gypsum

Calcium, Magnesium, Aluminium, and Ammonium of the sulphate salt affects the type and the severity of the attack. Therefore, use of supplementary cementitious materials together with cement results in the improvement of sulphate resistance of concrete. A common method to study the deterioration due to sulphate attack is discussed below.

To study sulphate attack on concrete, the cubes of concrete are cured for 28 days and then immersed in sulphate solution up to 28 days. After 28 days of immersion, the specimens are taken out and visually observed for the deterioration of the concrete due to sulphate attack. The specimens are weighed once again and the weight is compared with the normal concrete in order to calculate the percentage of loss of weight. Compression test is also conducted to assess the loss of strength.

After the study it was observed that the performance of the mixtures against sulfate attack can be arranged in descending order as silica fume, metakaolin, fly ash and control mortars. The higher performance of the pozzolanic mortars compared to that of control mixture is attributed to the reduction in cement portion of the mortars upon replacement of cement with the mineral admixture. As a result, C3A content of the binder reduces, consequently, the ettringite formation decreases. Besides, CH formation in the hydrated binder decreases due to reduction of C3S and C2S content of the binder. Besides, CH content of the hydrated binder reduces further due to the consumption of CH upon pozzolanic reaction. Furthermore, the formation of secondary C-S-H by the pozzolanic reaction, although less dense than the primary C-S-H gel, is effective in filling and segmenting large capillary pores into small, discontinuous capillary pores through pore size refinement. Thus, the total permeability of concrete decreases. As a result of this, transport properties are expected to improve. The similar improvements were obtained in the present study. Another reason for higher sulphate resistance of the mineral admixture-bearing mixtures is their lower permeability, which in turn, makes the ingress of the sulphate solutions difficult.

## C. Chloride ion penetration

Chloride ions are the primary cause for corrosion of reinforcement steel in concrete. Durability of concrete structure exposed to chloride environment is governed by the amount of chloride ingress into the concrete which heavily depends on the chloride concentration at the surface (C) and the diffusion coefficient (D) of the concrete. It is obvious that, diffusion of chloride ions into concrete takes place when there is sufficient moisture in the pore structure of the concrete.

They can penetrate faster when the moisture content in the concrete is high. The lower the moisture content in concrete, the lower the rate of chloride ingress into concrete, which in turn minimize the risk of deterioration caused by chloride contamination. Once the concrete is contaminated by chloride, the reinforcement steel in the concrete is highly susceptible to corrosion. The optimum relative humidity for corrosion is 70 to 80% that allows enough oxygen to diffuse into the concrete in order to initiate corrosion of reinforcement steel. The corrosion rate increases with increasing the chloride contamination rate and relative humidity, which in turn increase the risk of damage.

Chloride penetration can be assessed in the following method. Chloride solution is prepared by adding 3.5 % sodium chloride in distilled water. This solution is stirred well so that all the sodium chloride salts get dissolved in the solution. Weights of the cubes which are cured for 28 days are found before immersing. They are then immersed in a chloride solution for 28 days. After drying the cubes, the change in weight and also the compressive strength of concrete cubes are found.

In a study it was found that the amount of variation of diffusion coefficient D in concretes containing zeolite is lower than in the other concretes. However, after 9 months of exposing the specimens to chloride penetration, their diffusion factor decreases with an increase in the replacement levels of metakaolin and zeolite, while the amount of surface chloride increases with an increase in the replacement percentage of the pozzolans. This may be because these mineral additives form additional calcium aluminate hydrates in their reaction, which then combines with chlorides to form Friedel's salts. However the surface chloride content of concrete containing admixture was found lesser than ordinary concrete. The diffusivity factor of specimens containing SF decreases with an increase in the percentage from 5 to 7.5 and from 7.5 to 10. The diffusion coefficient in concretes with different water-tocement ratios is at least two times higher than in those containing pozzolans. However, the amount of surface chloride does not show any significant change with increases in the water-to-cement ratio, while it significantly increases with increases in Metakaolin. Also, increasing zeolite replacement from 10% to 20% sharply increases the amount of surface chloride from 20% to 30%. For SF, surface chloride increases when the SF replacement level increases from 5% to 7.5% and decreases when the SF replacement level increases from 7.5% to 10%. This can be attributed to the effect of the curing condition, due to the higher percentage of SF, the amount of cracks on the surface of the concrete increases, causing the value of D to increase and the value of C to decrease. The results obtained from the chloride content of specimens at a depth of 20 mm, were selected as the basis of comparison in order to obtain more consistent conclusions. For all concretes containing pozzolans, the amount of chloride at a depth of 20 mm was lower than that of recorded in the control mixture. In zeolite concretes, the higher the replacement level, the less chloride at a depth of 20 mm. A comparison of different w/c ratios shows that the amount of chloride at a depth of 20 mm increases with increases in the w/c ratio.

Another variable that has a significant influence in the chloride diffusion coefficient is the water/binder ratio. It was observed that, an increment in the water/binder ratio results in a severe increase in the diffusion coefficients. This is due to the fact that an increment in the water/binder ratio contributes to a greater number of pores and, above all, to a better connectivity between them.

Age also makes a strong influence on diffusion of chloride. A reduction in the diffusion coefficient for non-steady-state can be observed when moving from 28 to 90 days of curing. This reduction is a result of the pore refinement caused by the cement hydration development, and the increasing amount of available gel that can serve a place for chloride to bind. At 28 days, the incorporation of FA caused a rise in the value of the chloride diffusion coefficients for non-steady-states, which became much more significant at higher water/binder ratios. With increased hydration time (90 days) the value of the chloride diffusion coefficient diminishes considerably, becoming closer, or even smaller, to those of the control concretes. This reduction is caused by the advancement of the pozzolanic reaction, which has a pore refinement effect. It can also be noticed that the decline in the chloride diffusion coefficient goes hand in hand with the increase in quantity of fly ash used in the concrete.

Hence it was concluded that chloride penetration resistance was increased by addition of mineral admixture for both 56 and 90 day water curing. However blended mix has highest chloride penetration resistance followed by metakaolin mix and control mix.

# D. Sorptivity

Sorptivity is a measure of the capacity of the medium to absorb or desorb liquid by <u>capillarity</u>. Sorptivity can also be defined as an index of moisture transport into unsaturated specimens. Recently it has been recognized as an important index of concrete durability. During sorptivity process, the driving force for water ingress into concrete is capillary suction within the pore spaces of concrete and not pressure head. The method can also be used to measure the total pore volume of capillary and gel pores in the concrete. The sorptivity coefficient is essential to predict the service life of concrete as a structural material and to improve its performance. Several experimental investigations have shown that the capillary permeability is substantially affected by the curing condition. Sufficient curing is essential for a concrete to provide its potential performance.

For Sorptivity test cylindrical specimen of 100mm diameter and 50mm height is prepared. The specimen is then water cured. After curing, the specimen is oven dried and the weight is noted. The specimen is immersed in water with water level not more than 5 mm above the base of specimen and the flow from the peripheral surface is prevented by sealing it properly with non-absorbent coating. The weight is measured in a time interval of 30 minutes until the weight is constant.

At equal water/cement ratio, fly ash binary cement concretes have poor resistance against sorption and the resistance reduced with increasing content of fly ash. However, the resistance increased with increasing age such that at 180 days they became better than that of control mix concrete. Silica fume binary and ternary cement concretes have better

resistance to sorption than control mix and fly ash binary cement concretes at both early and later ages and their resistance increaseed with increasing content of silica fume. The sorptivity of concrete is influenced by strength. Compared with control mix concrete, the sorptivity of the cement combination concretes were lower at the equivalent strengths and they reduced with increasing total content of the cement additions.

Use of 30% FA reduced sorptivity of concrete by up to 40.8% at 180 days, while 0.6% PWC additive reduced sorptivity of concrete by a maximum percentage of 21.1% at 180 days. When both PWC and FA additives were used, sorptivity of concrete was further reduced, attaining up to 47.4% reduction at 180 days for 1.0% PWC + 30% FA proportion

#### E. Carbonation

Carbonation is associated with the steel reinforcement corrosion and with the shrinkage of concrete. In other words, it is the ability of concrete to protect steel from corrosion depending upon the extent to which the concrete of the cover zone is carbonated. Carbonation is a complex function of permeability and available lime.

Carbonation measurements are carried out for concrete cylinder of 150 mm diameter and 300mm diameter after exposure in a constant temperature of  $20 \pm 3^{\circ}$ C and  $65 \pm 5\%$  relative humidity in normal atmospheric conditions. The samples are broken into two halves at the age of 2 years. Phenolphthalein solution (Phenolphthalein 1% in Propan-2-ol) is sprayed on two fresh fracture surfaces. Colourless depth from the edge of the specimen is measured.

SF inclusion slightly increased the depth of carbonation as compared to the OPC control. The depth of carbonation significantly and linearly increased with an increase in FA content. For every increase of 10% FA content, the carbonation depth increased approximately by 0.3 mm. However, the maximum carbonation depth observed was about 2 mm, which is far less than the cover of reinforced steel bars to cause corrosion.

In another study it has been observed that the carbonation depth of concrete is bigger than the control mix in the case of *SF* or *MK*. The carbonation depth of *MK* concrete is 20 to 30% more than the control mix at 28 days for replacement level of 5% and 10%, however, 40% and 70% more carbonation depth at 56 days for replacement level of 5% and 10% has been observed. Similarly, large carbonation depths observed in *SF* concrete irrespective of the age and replacement level. Concrete mixed with *MK* and *SF* together, also demonstrated an increase in the carbonation depth with the increase of the replacement level. The reason for this increase in carbonation depth is that the *MK* or *SF* concrete possesses lesser content of portlandite in hydrate products due to pozzolanic reaction.

# F. Freezing and thawing action

Freeze and thaw is a natural phenomenon that causes deterioration of concrete in cold areas when water enters in the voids and get frozen. Voids are generally produced during the hydration of Portland cement, when calcium hydroxide leaches. Since concrete is a porous material and due to freezing of water to ice, increased volume of water in the

pores of concrete causes distress. This distress initiates with the first freeze-thaw cycle and continues throughout successive winter seasons resulting in repeated loss of concrete surface.

The resistance of cement to repeat cycles of freezing and thawing can be determined as per ASTMC 666, procedure A. This test can be terminated after 300 cycles, or when the specimen broke. In this test, the deterioration of specimens over time is measured using weight change and pulse velocity techniques. The weight change is used to indicate the amount of moisture that had been absorbed due to cracking caused by expansion of the cement paste. The pulse velocity readings were taken at four points around the perimeter of the specimen at each cycle and the average value is recorded.

At the end of 300 cycles, the reduction in compressive strength of the control, fly ash, metakaolin and silica fume mixtures were 26%, 18%, 11% and 7%, respectively. The weight loss for these mixtures was 1.36%, 1.05%, 0.7% and 0.48%, respectively. The weight loss of the specimen increased with increasing of the microcracks and scaling due to freeze-thaw cycles. Test results demonstrated that the mixture containing silica fume had the best performance against frost action. It should be mentioned that no air entraining agent was used in the mixtures. It is known that the degree of saturation of the material plays an important role in the freezing-thawing behavior. Thus, the transport properties can be a good measure of the freezing-thawing resistance of the material. Transport properties test results indicated that the permeability of the mortar mixtures decreased by using of the mineral admixtures. Moreover, the mixture containing silica fume had the best transport properties compared to the other pozzolanic mortars. As it can be seen from, the weight loss of the mortar mixtures exposed to 300 freeze-thaw cycles, increased linearly with increasing its water absorption capacity.

#### G. alkali silica reaction

Alkali–silica reaction (ASR) is a very trouble making reaction within concrete involving higher pH alkalis such as sodium and potassium hydroxide, which react with silica (usually exist within the aggregates) and produce gel. This gel has a high capacity of absorbing water from the pore solution causing expansion and disruption of the concrete. The main source of the alkalis is the Portland cement itself or external sources. According to ASTM C 1260, expansion due to ASR of less than 0.1% at 14 days of age indicates acceptable performance, while expansion of greater than 0.20% indicates unacceptable performance

Supplementary cementing materials are an effective means for controlling expansion due to alkali-silica reaction if they are used at a high enough level of replacement. The level of SCM required generally increases with the following parameters:

- The alkali available from the Portland cement increases (if significant alkalis are available from the aggregates—e.g. feldspars and greywackes or from external sources, this will likely also increase the level of SCM required)
- The alkali from the SCM increases
- The CaO/SiO2 of the SCM increases
- The reactivity of the aggregate increases

SCMs control ASR mainly by reducing the amount of alkalis available for reaction with the aggregate and the ability of SCMs to bind alkalis appears to be strongly related to the CaO/SiO2 ratio of the SCM. SCMs that are low in alkali and calcium, and high in silica tend to be the most effective in reducing pore solution alkalinity and these materials can be used at relatively low replacement rates to eliminate damaging expansion. SCMs with increased amounts of alkali and calcium have to be used at higher replacement levels.

From previous study it was observed that the calcium content of ASR products increased with time however concrete mixes incorporating Metakaolin and Silica fume showed lower expansion due to alkali aggregate reaction. SF and MK expanded 50% and 60% lesser than ordinary concrete. Also, addition of fly ash considerabily reduced the expansion.

#### **Conclusions**

From the previous studies it was observed that mineral admixtures greatly improved durability properties of concrete except carbonation. The study was mainly based on replacement of concrete with fly ash, silica fume, metakaolin and zeolite.

Zeolite has higher water permeation than Silica Fume or Metakaolin due to its permeability factor. The use of zeolite at 20% slightly increased the water absorption and porosity but increasing this percentage even more caused a slight reduction in water absorption. On the other hand, increasing the replacement percentages of SF and Metakaolin causes a small decline in water absorption and porosity. Moreover SF is influenced more by the curing condition than the other two pozzolans.

In case of sulphate attack it was observed that the performance of the mixtures can be arranged in descending order as silica fume, metakaolin, fly ash and control mortars. Chloride penetration resistance was increased by addition of mineral admixture for both 56 and 90 day water curing. However blended mix has highest chloride penetration resistance followed by metakaolin mix and control mix.

Positive effect of admixtures were observed with ageing in case of resistance against Sorptivity. In case of alkali aggregate reaction SF and MK expanded 50% and 60% lesser than ordinary concrete.

In case of freezing and thawing action the reduction in compressive strength of the control, fly ash, metakaolin and silica fume mixtures were 26%, 18%, 11% and 7%, respectively and corresponding weight loss for these mixtures was 1.36%, 1.05%, 0.7% and 0.48%, respectively

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