

Desultory notes on application of materials science to deciphering concrete durability

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We all know that Materials Science involves generation of knowledge relating to composition, structure and properties of materials. The science aspect focuses on discovering the nature of materials, which in turn leads to theories or descriptions that explain how structure relates to composition, properties and behaviour.

It is important to note that 'property' is, by and large, an outcome of the interaction between the 'character' (meaning the composition and structure) of one material with another and / or energy. 'Reaction' in this context, is a change of character with time and 'state' is an evaluation of 'character' from the perspective of the equilibrium theory. It is obvious therefore, that 'property' is unequivocally determined by 'character' and 'character' is estimated from 'property', when characterisation of materials and measurement of properties are suitably performed. In the characterisation it is necessary not only to know chemical and phase composition of micro area, the micro texture and the surface state but also to gather a wide range of information from micro to macro, besides understanding the average chemical and phase composition of the object. The recent development of analytical techniques and instruments for the above purposes is remarkable. It is almost imperative now to adopt and apply new techniques to the study of cement and concrete in general and their durability problems in particular. In this discussion I shall try to focus on the application of Materials Science to deciphering the durability problems (Figure 1).

A. CRYSTAL GROWTH PRESSURE

Let us concentrate on the crystal growth pressure in the deterioration of concrete.

A crystal, in direct contact with a supersaturated solution, grows in size and, if constrained, develops pressure against the constraint. This excess pressure is known as the crystal growth pressure which is expressed as

$$\Delta P = \frac{RT}{V_M} \ln \frac{a_s}{a_o}$$

where V_M is the molar volume of the crystals; a_s is the activity of the supersaturated solution; a_o is the activity of the saturated solution; R is the gas constant and T is the absolute temperature of the system. When the absolute concentration is low, a_i 's could be replaced by the corresponding concentrations c_i 's.

It should also be borne in mind that different faces of a crystal have generally different solubilities. The net result is that a crystal, in contact with a supersaturated solution, will grow along some direction and generate crystal growth pressures on some of its crystal faces even if it is free to grow in other directions without any constraints. The growing crystals which are within a structure develop crystal growth pressures and thereby induce tensile stress in the surrounding concrete.

For any breakdown to occur a concrete element must have a metastable assembly of crystals and a supersaturated solution may be produced by number of ways as exemplified below :

- a. When the anhydrous compounds have higher solubilities than the hydrous products, e.g., the solubility of hemihydrate in water is about five times that of gypsum and as such initially formed gypsum crystals are in contact with a supersaturated solution.

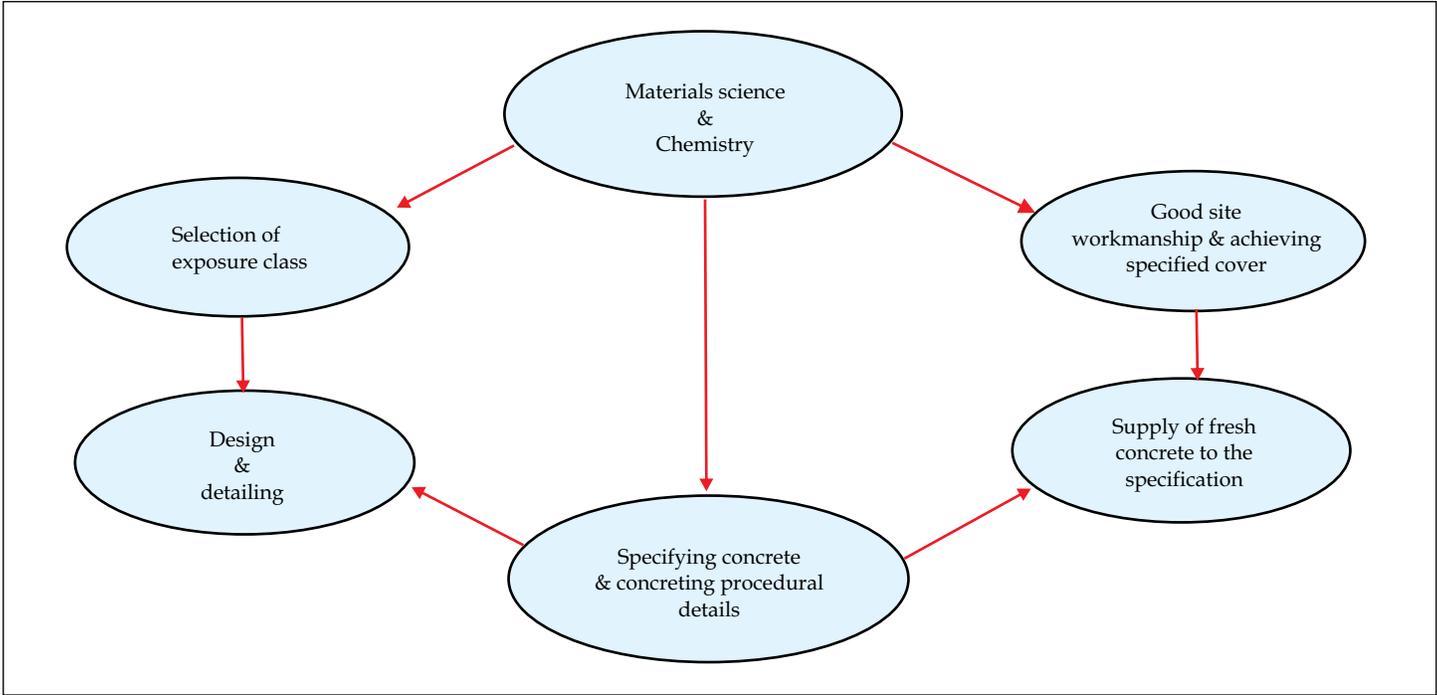


Figure 1. Common durability factors in all constructional domains and role of science

- b. When a precipitate has a wide range of particle size, the smaller crystals have higher solubilities than the larger ones so that the surrounding solution has a higher concentration than the saturated solution for the larger crystals.
- c. When evaporation of water is at a faster rate than the salt crystallisation.
- d. By fast cooling, it is possible to produce a supersaturated solution even in the presence of pre-existing crystals.
- e. Some salts such as sodium thiosulfate deca-hydrate can form metastable but highly supersaturated solutions.

It may be relevant to mention here that the actual damage of a concrete structure due to crystal growth pressure depends on the following parameters :

- i. The relative values of the effective crystal growth pressure and the tensile strength of the concrete.
- ii. The presence of a critical volume of the growing crystals.

- iii. The homogeneity or otherwise of the supersaturated solution within the concrete structure.

The evidence of the above factors in concrete damages can be observed in the concrete structure breakdown due to efflorescence, concrete damages due to the pressure of dead-burnt lime and magnesia, etc.

From the Materials Science angle let us recapitulate the concrete breakdown due to an oft-observed phenomenon of efflorescence. Of all the salts identified from efflorescence mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$) and thenardite (Na_2SO_4) are known to cause breakdown of porous materials but why !

From the temperature - RH diagram for the above phases and their solubility curves one may observe that below the critical temperature of 32.5°C there is a critical humidity above which thenardite is not stable and above 32.5°C mirabilite is not stable at any humidity. Now consider a concrete structure containing the critical volume concentration of thenardite at a temperature below the critical temperature of 32.5°C . If the RH of the environment is below the critical value, the thenardite crystals remain unaltered, though they are coated with a layer of its saturated solution. With increasing RH, on

reaching the critical value, mirabilite crystals nucleate and get surrounded by a supersaturated solution, and grow in size. If these growing crystals are constrained, they develop crystal growth pressure.

It is interesting to note that the concrete damage cannot be due to the volume increase during the conversion of thenardite to mirabilite, it being independent of the temperature at which the conversion may take place. The presence of a sufficient volume of the salt, a fluctuating temperature and/or moisture condition producing a super-saturated solution and a temperature below the critical value are necessary.

From the above discourse it is evident that the degradation and durability of materials in general and of concrete in particular involve measuring and understanding the effects of liquid and gaseous environments on their performance. Characterisation, phase equilibrium and phase transformations do provide an insight into the performance and degradation of such materials. This kind of appreciation of the application of Materials Science to Concrete Technology is extremely crucial and essential.

B. ION TRANSPORTATION IN CEMENT BASED MATERIALS SEEN FROM THE PERSPECTIVE OF MATERIALS CHEMISTRY

In this section I intend to highlight certain aspects of transportation of ions through cement-based materials from the perspective of electro-chemistry.

Transportation of both anions and cations through cement-based materials is one of the important processes in understanding their durability. Needless to mention that the subject has been studied quite extensively and such studies encompassed reinforcement corrosion, sulfate attack, alkali-silica reaction etc. But the question remains if these studies have given us some insight into the chemistry of ion migration through cement-based materials.

When we try to examine the diffusion of undissociated molecules, we take recourse to the Fick's laws of diffusion. By and large, it is understood that the Fick's first law of diffusion is applicable to a system in which the concentration of the diffusant is constant while the second law is applied to a system where the concentration of the diffusant changes with time.

The above two laws are valid only for an undissociated diffusant. In an ionic solution, the movement of ions is restricted by a strong electrostatic field caused by the other ions present in the solution. The restriction becomes particularly important when the diffusion occurs through a permeable barrier across which there is a concentration gradient. It has also been observed theoretically that the diffusion coefficient of an ion in such a situation decreases with the concentration of the solution used in an experiment. This, in turn, means that in the industrial measurement of a diffusion coefficient, the ionic concentration should preferably be chosen to be close to that of the real situation or else certain correction factor for the difference will have to be deciphered.

A concentration gradient of ions across a permeable barrier is generally accompanied by an electrical potential gradient. The gradient is known to hinder the diffusion of ion across the barrier. This is often regarded as a common problem in electro-chemistry. For steady-state diffusion there is a solution provided by Planck. However, in most publications on the diffusion of ions through cement-based materials, both the Nernst and the Nernst-Planck corrections have been ignored. Both the corrections become important in the case of weak acid attack on cement and concrete as well as in the determination of diffusion coefficients of ions using concentrated salt solutions.

As we all know, the measurement of the diffusion coefficient is done either by the diffusion cell technique or by the concentration profile technique. In the diffusion cell technique the steady-state conditions apply, while the concentration profile technique is applicable to the unsteady state conditions.

The volume of literature on ion migration through cement based materials is quite large. The salient observations of the reviewers on the migration of ions through neat cement pastes can be summarised as follows :

- Most workers have used the diffusion cell technique to study the steady-state model.
- It was difficult to compare the actual diffusivity values reported by different researchers. This is probably due to the variations in the type of Portland Cement, time, temperature and method

of curing, the nature and solution concentration of the diffusing salts, etc. There are several indirect indications that the ion migration through cement paste may not be a simple diffusion process.

Ion migration through Portland cement mortar and concrete has been studied by both the diffusion cell and the concentration profile techniques. The effects of different factors mentioned earlier on the diffusion process of mortars and concrete have not been studied as systematically as they were done for the pastes. A comparison of the results of investigations carried out with cement pastes and concrete samples show that the findings of paste samples are not consistent with those of concrete samples.

It is broadly presumed that the observed differences are due to the availability of an easier diffusion along the pastes-aggregate interface and presence of cracks. It may also be relevant to mention here that in the field concrete the interfacial zones are wider and the macro cracks are more numerous than what are obtained in small and well-cured laboratory samples. The increased defects in concrete may significantly increase the ion diffusion.

Let us now explore the reasons for some of the unusual characteristics of ion migration such as the higher diffusivity of Cl^- ions than that of alkali metal ions in Portland cement pastes as well as high activation energies of ion diffusion through ordinary Portland cement pastes.

It is well known that the cement hydration products have very high specific surface and they along with the aggregates in concrete are surrounded by a highly alkaline pore solution. From the colloid chemistry angle it would be expected that some of the properties of cement pastes and concrete will be determined by the interaction between the hydration products and the electrolyte solution that surrounds them and more particularly by the electrical double layers that form around the hydration products.

The characteristics of the double layer suggests that during the diffusion of a neutral salt, e.g. NaCl, the negative ions diffuse through the bulk solution, in which their concentration is higher and the positive ions diffuse mainly through the double layer. This is particularly so in low w/c pastes, the reasons being the general narrowness

of the transport channels. In the wider transport channels both the normal diffusion and the double layer diffusion occur simultaneously. It has been experimentally observed that there is a higher concentration of Ca^{2+} ions in the Gouy-Chapman layer and it ensures that Ca^{2+} co-diffuse with Na^+ ions in the same ratio of their relative concentrations in the double layer. This co-diffusion of Ca^{2+} ions is taken as the basic explanation of the observed difference in the diffusivity between alkali and chloride ions.

In the case of a Portland cement paste, the high Ca^{2+} ion concentration in the Gouy-Chapman layer is maintained by the dissolution of calcium hydroxide in the case of composite cements with high content of mineral admixtures, the high Ca^{2+} ion concentration in the double layer cannot be maintained due to lack of calcium hydroxide in the paste. This apparently results in near equal diffusion of alkali and chloride ions through these pastes.

Coming to the observed high activation energies of ion diffusion in the Ordinary Portland cement pastes, one finds some explanation in the linked processes of diffusion. These processes have the following trends :

- Linked migration of positive and negative ions.
- Linked processes of dissolution of calcium hydroxide and migration of Ca^{2+} and OH^- in opposite directions,
- Maintenance of high Ca^{2+} concentration in the double layers,
- Linked formation of the Friedel's salt ($\text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 11\text{H}_2\text{O}$).

From the above simplified narration without providing the back-up experimental findings of various researchers published from time to time in the literature, one may observe that the formation of the electrical double layer and ion diffusion through the double layer explain a number of previously unexplained observations. It is, thus, obvious that the Materials Science of cement and concrete in general and in-depth understanding of physical chemistry and electrochemistry in particular are of great help in understanding the complex ion diffusion process.

Therefore, once again we unhesitatingly emphasise the essentiality of applications of Materials Science to Concrete Technology.

C. CHLORIDE ATTACK ON CONCRETE FROM THE PERSPECTIVE OF CHEMISTRY

Chlorides are known to degrade all concrete structures either by directly attacking the concrete itself or via the process of corrosion of its reinforcing bars. The chemistry behind these two modes of degradation is quite different. In this section my intention is to go back to the basics of direct chloride attack on concrete.

Depending on the cations, the chlorides behave quite differently with lime-riched Portland cements. Chlorides such as hydrochloric acid (HCl), ammonium chloride (NH₄Cl), aluminium chloride (AlCl₃), ferric chloride (FeCl₃) and magnesium chloride (MgCl₂) are either acidic or behave in an acidic manner in their interactions with Portland cements. In the process they form either water or volatile ammonia or ultimately soluble calcium chloride (CaCl₂), and gels of silica, alumina and iron hydroxide. In the case of magnesium chloride attack, gels of magnesium hydroxide and basic magnesium chloride are formed. There are hardly any protection against these chlorides, even if they are in a dilute state. It has, however, been reported that gels of magnesium hydroxide and basic magnesium chloride form a somewhat rate retarding layer on concrete.

Alkali and alkali earth chlorides are known to behave quite differently. Let us specifically look at the effects of alkali chlorides and calcium chloride on concrete durability, as other alkali earth chlorides do not find large-scale use in concrete construction and studies on their actions are also sparsely reported.

At room temperature the solubility of calcium hydroxide in alkali chloride solutions first increases with concentration and then decreases. At a given alkali chloride concentration the solubility of calcium hydroxide increases with decreasing temperature. The resultant effect, of course, is leaching of calcium hydroxide from the hardened cement paste. Under certain conditions this leaching may result into an increased porosity level of a Portland cement concrete structure.

Apart from dissolution, the leaching of calcium hydroxide may be caused by alkali chlorides through the diffusion process as well. It has been observed that the diffusivity of chloride ion is almost ten times higher than that of the alkali ions. The actual diffusivity of Cl⁻ depends on its cations and decreases in the following order Ca²⁺, Li⁺, K⁺ and Na⁺.

The system Ca(OH)₂ - CaCl₂ - H₂O has been studied quite extensively. There are two ternary phases in the system: Ca(OH)₂ · CaCl₂ · H₂O and 3Ca(OH)₂ · CaCl₂ · 12H₂O. The first one forms at a higher concentration of calcium chloride than the second one. The phase 3Ca(OH)₂ · CaCl₂ · 12H₂O crystallises below 30°C and its stability decreases with increasing temperature. On the other hand the stability of Ca(OH)₂ · CaCl₂ · H₂O increases with temperature.

The above compounds are quite sensitive to the presence of CO₂. In the pseudoquaternary system Ca(OH)₂ - CaCl₂ - CO₂ - H₂O the existence of CaCl₂ · 2CaCO₃ · 6H₂O has been reported, which crystallises at about 25°C and its solubility decreases with decreasing temperature.

What is more widely known is the formation of Friedel's salt (C₃A · CaCl₂ · 10H₂O) due to the interaction of alkali chlorides with the tricalcium aluminate phase of the cement. The system C₃A - CaCl₂ - H₂O is also known to have the existence of a high-chloride chloroaluminate (C₃A · CaCl₂ · 30H₂O) in 21 - 23 per cent calcium chloride at -10°C. This ettringite analogue is unstable both at 20°C and in saturated calcium hydroxide solution, converting into the Friedel's salt.

Most of the early work on the chloride attack on concrete have been carried out in connection with their use as the de-icing agents. It is generally understood that sodium chloride causes less damage to Portland cement concrete than calcium chloride. In the 1970's it had been shown that the concentrated solutions of calcium chloride severely attacked Portland cement mortar specimens at the room temperature; however, identical specimens stored in comparable concentrations of sodium chloride solutions remained undamaged. It had also been experimentally observed that the severity of calcium chloride attack increased as the temperature was lowered from 40° to 5°C. The experiments conducted then revealed that the

compressive strengths of mortar specimens remained unaffected during their storage in sodium chloride at all temperatures and concentrations, but those stored in calcium chloride solutions showed differences in compressive strengths, depending on concentration and storage temperature. At 20°C only a 30 per cent calcium chloride solution caused a decrease in strength, while 5 and 15 per cent solutions had no effects. At 40°C a 30 per cent solution of calcium chloride caused a small reduction in strength but unlike the previous case, the strength losses at 20° and 5°C were much more severe.

In terms of the phase formation, it was observed that in the temperature range of 5 to 40°C and at concentrations ranging from 5 to 30 per cent the Friedel's salt formed at all temperatures and calcium chloride solutions. Another unidentified complex phase was reportedly observed, involving calcium chloride, calcium hydroxide, calcium carbonate and water, at lower temperatures and higher concentrations of calcium chloride only.

The difference in the aggressiveness of sodium chloride and calcium chloride solutions at the room temperature has been explained by some investigators by the fact that the concentrated solution of calcium chloride is acidic and that of sodium chloride is neutral. This theory has been doubted by other investigators as the mortar specimens dissolved in calcium chloride solutions did not show the complete dissolution of the cement phases. Other researchers have tried to explain the relative aggressiveness of calcium chloride solution with the help of new phase formed, as mentioned earlier, and exertion of crystal growth pressure of these phases on the surrounding paste.

Many other data tend to establish that the Friedel's salt could not be associated with the concrete destruction process. Mortar specimens stored in saturated sodium chloride solution at 50°C remained undamaged even after 10 years inspite of the abundant formation of the Friedel's salt, as reported by some investigators. Similarly, the phase $\text{Ca}(\text{OH})_2 \cdot \text{CaCl}_2 \cdot \text{H}_2\text{O}$ could not be associated with the observed breakdown of concrete.

The expansion and breakdown of concrete could therefore be explained on the basis of the formation and crystal growth of the complex basic chlorides. The breakdown

process is apparently aggravated by the anisotropic growth habit of the acicular crystals of $3\text{Ca}(\text{OH})_2 \cdot \text{CaCl}_2 \cdot 12\text{H}_2\text{O}$. At temperatures above 30°C these crystals do not exist and hence the concrete samples remain undamaged. The absence of any basic calcium chloride phase in the cement mortar specimens immersed in sodium chloride solutions explains why there is no damage to concrete in such situations at all temperatures. The role of the carbonate bearing chloride complexes in the concrete breakdown process is still not clearly understood.

In field concrete such initial crystallisation may occur in the pre-existing cracks or defects. During their continued growth these crystals are likely to exert tensile stress on concrete around them and cause cracks, which often go through the interfacial zones. If this mechanism is really operative, then air-entrainment may provide some stress-free space, where the salt crystallisation may occur without causing any damage.

It may also be relevant to mention here that not much of systematic studies have been reported on the effects of concentrated chloride solutions on concrete made with composite cements. However, some studies have shown that concretes made of composite cements with either high pozzolanic material or very high slag content and having no free calcium hydroxide in the system could withstand the effects of 30 per cent calcium chloride solution at even 5°C without any damage.

Thus it appears that the exposure of concrete structures to chlorides is an object of complex study in Materials Science and Chemistry. Much has been studied, yet much remains to be explored and understood. But its importance and relevance can not be underestimated.

D. PHYSICS OF DRYING SHRINKAGE AND CREEP OF HARDENED CONCRETE

Although the elastic and thermal deformation of concrete have been known for quite some time, it is only relatively recently that the importance of creep and drying shrinkage have been recognised for their practical significance. In simple terms, as we all know, the drying shrinkage refers to a net decrease in volume of concrete due to the removal of water without any imposed load. Creep, on the other hand, is a measure of volume change due to an imposed

load - either uniaxial or multiaxial. However, creep and drying shrinkage may often occur together, thereby altering the dimensional change in the loading direction.

Broadly, there are two theories to explain the shrinkage mechanism - one is known as the "capillary tension theory" and the other is referred to as "the theory of disjoining pressure". Before we come to these theories, we may note that in a drying environment where a relative humidity gradient exists between the concrete and surrounding air, free water is initially lost from the larger capillaries and little change in volume or shrinkage occurs. However, this creates an internal humidity gradient, which causes adsorbed water to be transferred from the gel pores and interlayer water to be moved to the larger capillaries.

This process results in a reduction in volume of the C-S-H caused by the compression of its solid skeleton by the capillary tension set up by the increasing curvature of the capillary menisci. This is generally referred to as the capillary tension theory. The theory of disjoining pressure is applied to areas of hindered adsorption of interlayer water. The removal of this water causes a reduction in pressure and hence, a reduction in volume.

It has also been suggested in the literature that there is a third mechanism for situation of lower relative humidity. In such cases, the change in surface energy of the C-S-H due to the removal of the firmly held adsorbed water molecules is thought to be responsible for the reduction in volume or shrinkage.

It may be relevant to mention here that although the above theories are applicable to the reversible situations, the shrinkage process is not fully reversible, perhaps due to the formation of additional bonds during the drying process as well as due to the occurrence of the carbonation shrinkage that prevents ingress of water on re-wetting.

The exact mechanism of creep is still not very clear. The basic creep appears to be related to the internal movement of adsorbed or interlayer water, as concrete devoid of all evaporable water exhibits little creep. Internal movement of water may occur because all the pores do not remain full of water. Further, the observed dependency of basic creep on porosity or strength is treated as an indirect evidence of the empty pores being the governing factor for the occurrence of creep.

The long term creep, after all the water has disappeared, may be due to the viscous flow or sliding movement of the gel particles. If every volume element of a concrete specimen is occupied by solid cement hydration products, anhydrous cement particles, aggregates or the pore solution, i.e., without any volume occupied by air or water vapour, then a triaxial or hydrostatic loading of the sealed sample should produce a creep that is primarily determined by the compressibility of the components mentioned above.

In any case the net volume decrease is expected to be very small under realistic loading that is encountered in concrete structures. Under uniaxial loading the creep of a fully saturated and sealed specimen in the loading direction will be nearly compensated by a corresponding change in other two directions.

The first drying shrinkage of concrete decreases with increasing aggregate content. Using a model of spherical elastic particles embedded in a paste matrix, Pickett derived an equation relating drying shrinkage of a cement paste and that of concrete containing that cement :

$$S_c = S_p (1 - V_a)^n$$

Where S_c is the shrinkage of concrete

S_p is the shrinkage of the cement paste

V_a is the volumetric fraction of the aggregate

n is a constant for mixes of constant water/cement ratio

While Pickett had found n to be 1.7, many other researchers measured it in the range of 1.2 to 1.7.

In this context it is worthwhile to note that the greater the volume of aggregate, the lower the shrinkage. One may compute that increasing the aggregate content from 71 to 74 per cent will reduce the shrinkage by about 20 per cent. As could be anticipated, for a constant volume of aggregate, shrinkage increases as the water/cement ratio increases. One should also observe that the lower the relative humidity, the greater the shrinkage because of the higher humidity gradient between the concrete and the environment. Finally, the stiffer the aggregate, the lower the shrinkage of the concrete.

Two other parameters are worth mentioning, viz., the drying time and size of the member. It has been

indicated in the literature that typically, as a proportion of 20-year shrinkage, 20 per cent occurs in 2 weeks, 60 per cent in 3 months and 75 per cent in one year. As a result the occurrence of shrinkage, which is initially high, rapidly decreases with time. So far as the element size is concerned, the effect can be expressed in relation to either the volume/surface ratio (V/S) or the effective thickness ($2V/S$), which represents the average drying path length. The determining parameter obviously is the surface area of the member exposed to drying.

In normal concrete structures the drying shrinkage can be as high as 600×10^{-6} which is about six times as high as the failure strain in tension. Consequently, if shrinkage is restrained, cracking can take place. Shrinkage also causes a loss of pre-stress in pre-stressed concrete and increases deflections of asymmetrically reinforced concrete.

The source of creep in concrete is the hardened cement paste since good quality normal weight aggregate does not creep at the levels of stress existing in concrete. The role of the aggregate is to restrain the creep of the paste, as it does for shrinkage. Similarly, for drying concrete, creep is greater, the lower the relative humidity of the surrounding environment. Like drying shrinkage, creep of drying concrete is affected by the size of the member.

In general there is a direct proportionality between creep and the applied stress. It is approximately proportional to the stress/strength ratio, the upper limit being 0.5 – 0.6. At higher levels microcracking plays an important role and the long-term effect is the time-dependent creep rupture.

In the context of repair and renewal of concrete buildings one may broadly presume that the effects of creep are disadvantageous in concrete structures. It increases the deflection of reinforced concrete beams and causes a

loss of prestress in prestressed concrete elements. Creep may also cause excessive deflection in tall buildings and long bridges. Cracking of partitions and failure of rigidly fixed external claddings can occur due to differential movement. In mass concrete, when it undergoes a temperature fluctuation due to heat of hydration and cooling in a restrained state, creep may turn out to be a cause of cracking.

Notwithstanding all the above negatives, creep has a beneficial role in the sense that in all concrete structures it reduces the internal stress due to non-uniform or restrained shrinkage with the resultant reduction in cracking.

Drying shrinkage and creep of concrete are of immense significance in modern construction. Its understanding in relation to the cement paste, aggregate, strength, porosity and member dimension is quite important, relevant, and crucial. The literature on the subject is voluminous and it is interesting to note that almost every researcher has proposed his own mechanism for creep. Many of these mechanisms are related to their structural models of hardened cement paste. Many of the studies have been done with specimens containing extensive cracks and voids or under irrelevant relative humidity conditions. Hence, the much-studied subject apparently demands more precise investigations, yielding practically applicable models.

CONCLUDING REMARKS

The four topics dealt with in this discussion are obviously only illustrative. They only offer a flavour of application of Materials Science to concrete durability evaluation. The present state of Knowledge in the aforesaid topics should provoke young scientists to delve into advanced research in the fields.



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