STRUCTURE - PROPERTY RELATIONSHIP IN CONCRETE

by A. de S. Jayatilaka & H.S. Paul

Introduction

Concrete can be considered a complex, heterogenous multiphase material. It consists of aggregate embedded in a matrix of hardened cement paste. The structure of concrete which reflects its behaviour is often overlooked. This paper aims at emphasising the importance of structure property relationships.

An attempt to understand the structure of concrete without being aware of that of hardened cement paste will not meet with success. Much emphasis is therefore laid on the structure of hardened cement paste in this review.

The production of a new type of concrete on an empirical basis without understanding the structure can prove to be both dangerous and expensive. This was made clear in the observed failure of high alumina cement structures with age. High alumina cement and ordinary Portland cement were observed to have more or less the same strength initially. A study of the structure revealed that the products of hydration of high alumina cement were metastable and transformed with time to a more stable product. This transformation it was observed was accompanied by a reduction in volume of the products of hydration which in turn increased porosity drastically, thereby reducing the strength. The obvious advantages of investigating structure-property relationships thus become clear. The development and understanding of structure property relationships will steer future research in the right direction. Vast amounts of resources spent on research can thereby be geared to the development of an 'ideal' composition.

Hardened Portland Cement Paste

Mechanism & Products of Hydration[1]

Concrete is prepared by mixing together cement, water and aggregate. The aggregate is generally considered an inert material but its presence affects both the strength and durability of concrete.

The four main constituents of portland cement are :-

Tricalcium Silicate - $3\ CaO.SiO_2$

Dicalcium Silicate - $2\ CaO.SiO_2$

Tricalcium Aluminate - $3\ CaO.Al_2O_3$

Tetracalcium Aluminoferrite - $4\ CaO.Al_2O_3Fe_2O_3$

In addition there are small quantities of magnesium oxide, potassium oxide, gypsum, etc.

The main products responsible for the hydration of cement are dicalcium silicate and tricalcium silicate, while the aluminate and ferrite do not play such a significant role.[2]

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The mechanism of hydration involves the hydrolysis of calcium silicate which yields a supersaturated solution of calcium hydroxide. Ettringite and calcium hydroxide precipitate out, and a dense gel coats the grains simultaneously. This coating inhibits the reaction of the cement with the environment leading to a dormant period.

The gel coating subsequently ruptures possibly due to differences in osmotic pressure within and without the coating. The protrudes grow into fibrils and finally into a network if intertwining fibres which serve as a matrix for the aggregate and unreacted cement.[3-7] Figure 1 shows the stages of hydration of a cement particle.

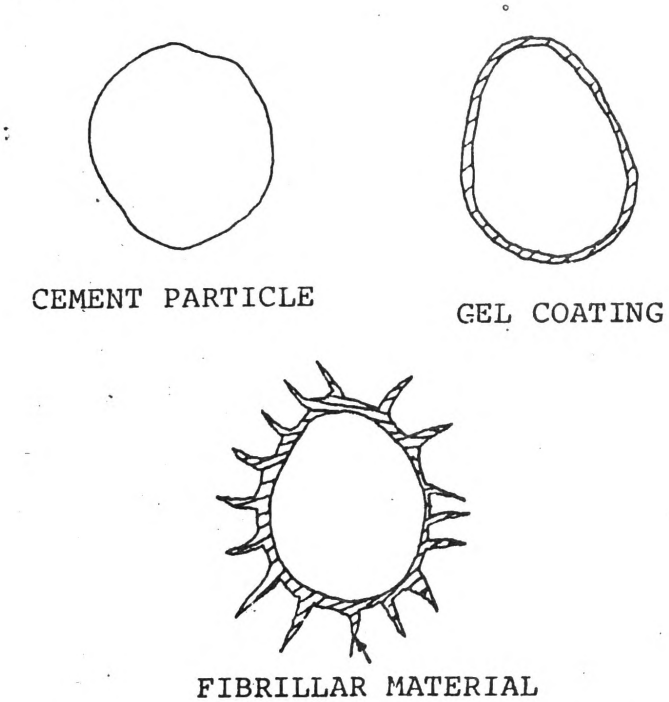


FIG. 1 DIAGRAM SHOWING MECHANISM OF HYDRATION

Double and Hellawell[3,6,7] showed a parallel between the hydration of the cement and the formation of silica gardens when an aqeously soluble salt Cobalt Nitrate is in contact with sodium silicate.

The products of hydration include[3]

a. Calcium Silicate Hydrate gel
b. Crystalline Calcium Hydroxide
c. Ettringite
d. Calcium Aluminate Monosulphate Hydrate
e. Unreacted cement.

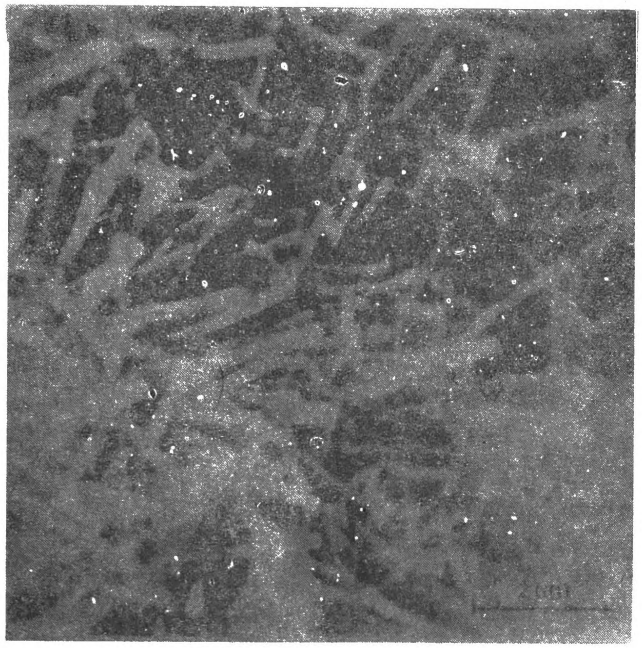


FIG. 2 (a) "PHOTOMICROGRAPH OF FIBRILLAR MATERIAL AND $Ca(OH)_2$ PLATELETS"

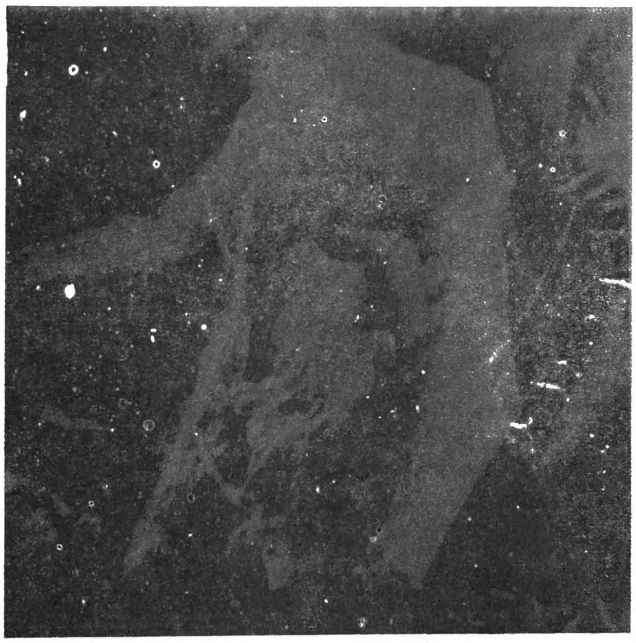


FIG. 2 (b) PHOTOMICROGRAPH OF CALCIUM HYDROXIDE PLATELETS

The chief products of hydration are the calcium silicate hydrate gel and the calcium hydroxide. (see figure 2 (a) and 2 (b)). These two main constituents control the properties and behaviour of concrete when used structurally.

Structure of Hardened Cement Paste

Various suggestions have been made regarding the atomic arrangement of the gel, based on electron microscopy, x ray diffraction and sorption studies. The only conclusion that can be drawn is that the gel is a three dimensional colloidal network.[4,8]

The gel has been observed to consist of monomers, dimers, trimers and more highly condensed species. The character of the gel changes with age and Tamas[10] concluded that only a small amount of highly condensed species are to be expected.

Surface area normally refers to the external bounding area of a particle. In calcium silicate hydrate gel, surface areas are so high that they must include internal surfaces within particles and on such a scale that makes internal surfaces a predominant feature. The gel is therefore complex both compositionally and structurally.[8]

The structure of hardened cement paste can also be viewed at the atomic, microscopic and macroscopic levels.

The atomic constituents include crystalline phases (calcium hydroxide, residual cement), quarzi amorphous phases (calcium silicate hydrate gel) and amorphous phases (organic additives and the hydration products of tri calcium aluminate).[8]

Viewed at the microscopic level, elongated fibrillar material are observed radiating from the gel initially. They are usually about 0.5 to 2.0 mm long and less than 0.2 mm across. They are usually not parallel and taper towards the end. They tend to branch at the tip, shorter fibres having a greater tendency to do so.[8,9]

The amorphous nature of the gel is confirmed by Transmission Electron Microscope studies which show that the fibrillar material consist of hollow tubes, which are not faceted. This fibre like structure is a major contributory factor to the toughness of the gel.[8]

It is difficult to see in detail with advancing maturity, i.e. no individual particle morphology can be seen. The gel is thus viewed as a continuous system with water filled and dry capillary pores.[8,10]

Concrete at the macroscopic level could be likened to a composite.[3]

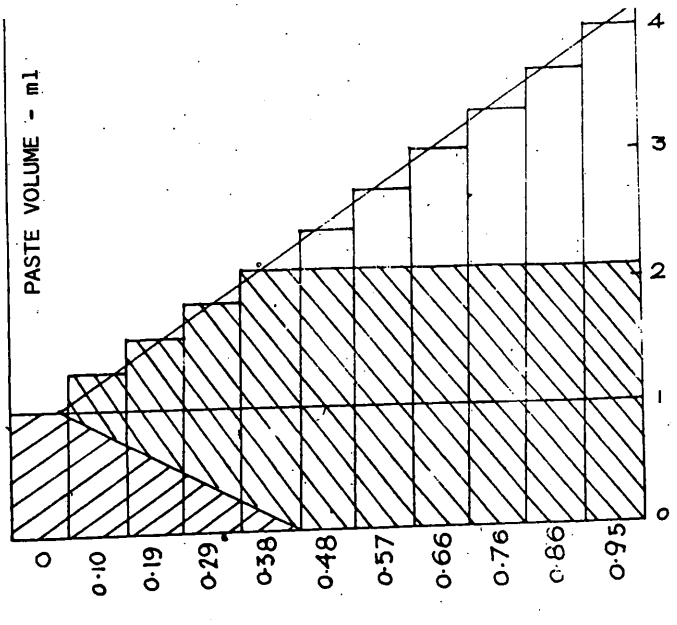
Pore Size, Distribution and Control of Pore Volume

Besides the hydration products of cement, pores, cracks, aggregate and unhydrated cement have been observed in the microstructure of concrete. Each of these constituents affect the behaviour of concrete, and the effect of porosity appears to be significant.

Pores refer to the spaces surrounding and within the network containing water. The porosity and the pore size distribution are not intrinsic properties of the paste, but are dependent on the water/cement ratio, degree of hydration, degree of compaction, etc.[8]

Pores fall into two categories, namely capillary and gel pores. The former refer to the original water filled spaces, while the latter refer to the interstitial voids within the gel itself. The former are generally much larger than the latter. The actual size of the capillary and gel pores have been estimated at 18°A and 8°A respectively.[4]

To eliminate excessive porosity, a minimum amount of water should be used. The volume of the products of hydration is nearly twice that of the unhydrated cement.[11] It is obvious from figure 3 that at water/cement ratios greater than 0.38, even if 100% hydration were to occur, the products of hydration cannot fill the entire volume of water filled spaces. The obvious conclusion is that the higher the water/cement ratio, the higher the porosity and the lower the strength.[3]



WATER/CEMENT RATIO BY WEIGHT COMPOSITION

OF CEMENT PASTE AT 100% HYDRATION

FIG. 3 WATER CONTENT VS. DEGREE OF HYDRATION

Categorisation of Water in Cement Paste

Water in cement paste can be categorised as [1] -

a) Chemically Bound Water, which refers to water present in the hydrated compounds
b) Gel Water, which is water adsorbed on the surface of the gel
c) Capillary Water, which refers to water present in the paste but beyond the range of surface forces.

The water content depends on the relative humidity. The gel water is retained even at very low humidities, whereas the capillary pores empty no sooner the relative humidity falls below 45%.[1]

The water present in these pores makes concrete susceptible to creep when under compression. This is as a result of the motion of water. Besides evaporation of water from within the pores leads to shrinkage, which in turn leads to microcracking and a reduction in strength.

Models for Hardened Cement Paste

Information available on the products of hydration of cement is insufficient to arrive at a conclusive description of the structure of hardened cement paste. This has led to the development of models. Models enable the actual complex situation within the gel [4,10] to be described in a simple manner.

Models developed today are of two types[4]

a. Inductive Models

These are constructed by taking into account all relevant information such as pore size, pore size distribution, mutual interaction of colloidal particles and characteristic properties of absorbed water films. The validity of such a model must be checked by a critical comparision of the predictions with the observed behaviour.

b. Deductive Models

These are based on experimentally determined macroscopic data. These have to be tested by carrying out more fundamental work on the structure.

The models put forward todate include the Powers Brunauer Model, Ishais Model and the Feldman Sereda Model.

Power Brunauer Model[4,5,10,12]

This model is based on a classification of the water held (see Fig. 4). It assumes that the gel is similar to the products of hydration of di calcium silicate and tri calcium silicate. It further states that the gel has a very high specific surface of the area of the order of 180 m^2/g, with a minimum porosity of 28%.

The pores present are classified as gel and capillary pores. The minimum porosity (28%) is attributed to the gel pores (visualised as pores between gel particles) of which the solid to solid distance is in the range of 15-18°A. The gel pores are assumed to be accessible only to water molecules as entrances to these pores are less than 4°A.

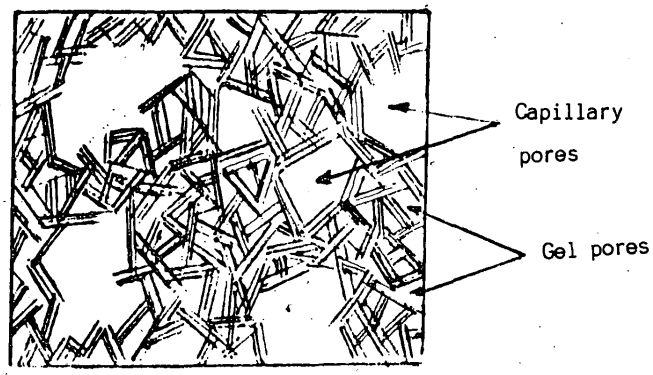


FIG. 4 POWERS BRUNAUER MODEL

Any space not filled with gel is termed capillary space, and these bigger pores (20-40°A) are remains of the original water filled spaces. The volume of these pores depends on the water/cement ratio and the degree of hydration.

The other features of this model are the colloidal nature of the gel (dimensions around 100°A), its porosity and the importance of water in determining its behaviour. The particles are supposed to be held together by van der Waal's forces and the presence of chemical bonds between particles is also suggested. The exact location and function of these bonds has not been understood.

Ishais Model[5,12]

This model is based on research carried out at Technion, Israel Institute of Technology and is based on Power Model, but with a difference in the classification of waterheld (see Fig. 5).

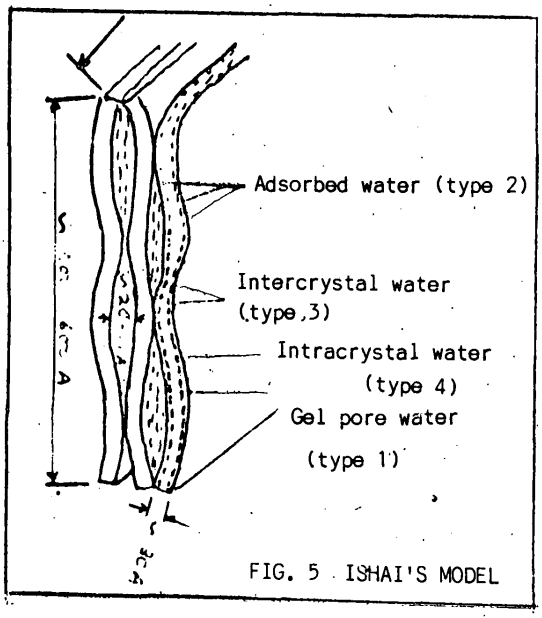


FIG. 5 ISHAI'S MODEL

This model distinguishes four types of evaporatable water -

a. Water present in the gel and capillary pores which are beyond the range of action of surface forces, i.e. water distance more than 10 - 20° A from the surface.

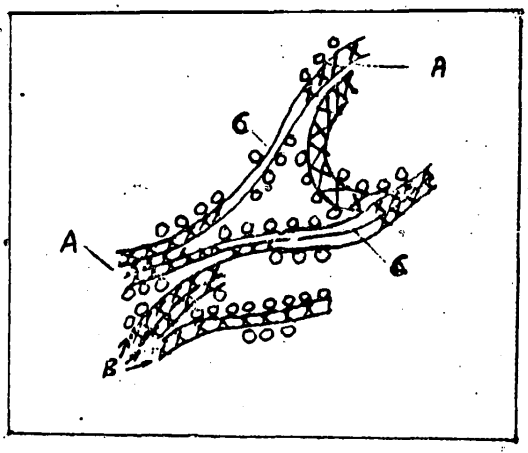
b. Water adsorbed on the surface of the calcium silicate hydrate crystallites at a distance of 4-8°A from the surface.

c. Adsorbed water confined between adjacent crystallite surfaces in narrow spaces not greater than 8°A. This type of water is subjected to two sets of forces - the normal adsorption force coupled with a compressive force and is therefore more strongly held

d. Intracrystalline water which is a strongly bound layer one molecule thick, in between the layers of calcium silicate hydrate crystallites.

Feldman Sereda Model[5,10,12]

This model assumes that the calcium silicate hydrate gel is a poorly crystalised version of a layered silicate (as shown in figure 6). It proposes that the role of water is much more complexed. The main features of this model are interlayer water and its importance in explaining the behaviour of concrete.



(A interparticle bond; X, interplayer hydrate water; C CSH sheets; O, physically adsorbed water)

FIG. 6 FELMAN SEREDA MODEL

The gel particles were thought to be crumpled sheets made up of two to four layers of molecules. Water in contact with the dried gel

a. interacts with the free surface forming hydrogen bonds;

b. is physically adsorbed on the surface;

c. enters the collapsed layered structure of material at lower temperature and

d. fills the large pores by capillary condensation at higher humidities.

This model considered the water present in inter layer spaces as part of the structure, being more organized and contributing to the rigidity of the system. Most of this water is removed from the structure at relative humidities of less than 10%. This structural water is not considered as pore water. According to this model gel pores as such do not exist. The total porosity can be obtained by fluids that do not cause interlayer penetration. The surface area of the gel varies from 1-150m^2/gm depending on the method of preparation.

Discrepancies do exist among the models suggested todate. Ishai distinguishes four types of evaporatable water. Powers defines type (a) as capillary water and types (b) and (c) as gel water. The concept of intracrystalline water (Type d) is overlooked altogether though it's presence was suggested way back in 1955 by Kalousek. He suggested that the volume of pores is approximately equal to the evaporatable water content. In contrast the layered structure of the gel suggests that a part of the water is intracrystalline, i.e. it may be considered an integral part of the solid. If such were the case, the pore content is not equivalent to the volume of evaporatable water, but lesser and Powers model no longer holds. Models are thus no actual representation of reality.

Properties of Concrete

Toughness

Concrete is somewhat a brittle material, though not exactly so. All brittle materials fail suddenly at a critical stress and the failure is generally catastrophic. This is due to the rapid propagation of cracks when tensile loads are applied.[13-15] A characteristic feature of concrete is slower crack extension prior to failure.[16-26]

In cement paste the hexagonal platelike structure of Calcium Hydroxide behaves as cleavage planes.[3] There is hence rapid propagation of cracks in cement paste compared with concrete. In the latter, the aggregate may initiate subsidiary cracks, cause branching of cracks or cause the cracks to circumvent the aggregate. This results in slow crack growth which explains the higher toughness of concrete compared with cement paste. The coarse aggregate is the main factor responsible for the above.[3]

Strength

The aggregate-matrix bonds have a significant effect on the strength of concrete.[3]

Cement paste shrinks mainly due to the evaporation of water, the mechanism however, being not fully understood.[23-25] The increase in Van der Waal's forces caused by the evaporation of water may be a probable cause. This may be true of gel pores, but does not hold in the case of capillary pores where the range of action of these forces is insufficient. Carbonation (i.e. $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3$) may also be a source of shrinkage.

Aggregate does not shrink and inhibits shrinkage at the interface, producing interfacial stresses. If these stresses exceed the bond strength they result in the formation of cracks.[3,12] Large pores present in concrete also serve as cracks.

Cracks affect the strength of concrete significantly. Cracks can propagate through the matrix, through the aggregate

or otherwise along the aggregate matrix interface, the latter being the most likely. According to Griffiths criterion the fracture strength of concrete is inversely proportional to the semi-crack length.[3]

The stress strain curve of concrete under compression shows inelastic behaviour (as shown in Fig. 7). This can be attributed to the formation of micro cracks, which in turn decreases the rigidity of the specimen.[3]

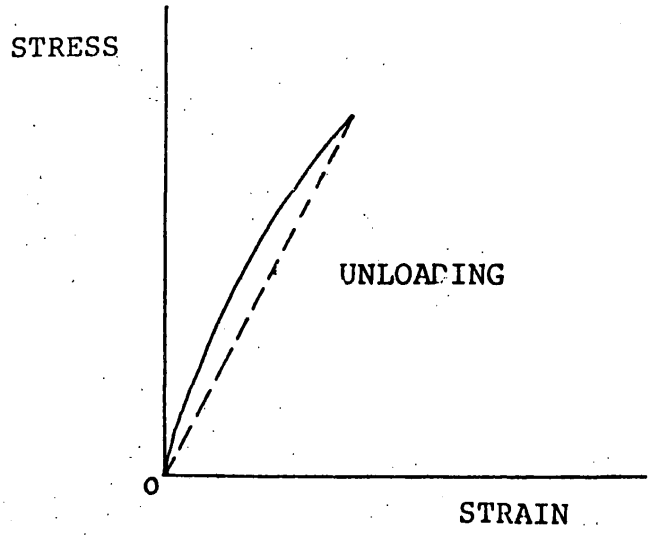


FIG. 7 STRESS- STRAIN CURVE FOR CONCRETE

The water/cement ratio, W/C, which in turn affects the gel/space ratio also exerts a controlling effect on the strength (see Fig. 8). The Youngs Modulus E of concrete decreases with increase in porosity. According to the Griffiths criterion, this reduces the fracture strength σ_f significantly. The fracture strength σ_f is given by

$$\sigma_f = \frac{(2E\gamma_f)^{\frac{1}{2}Y}}{\pi a}$$

Where Y = geometrical factor which depends on the geometry of the specimen
γ_f = work of fracture
a = semicrack length

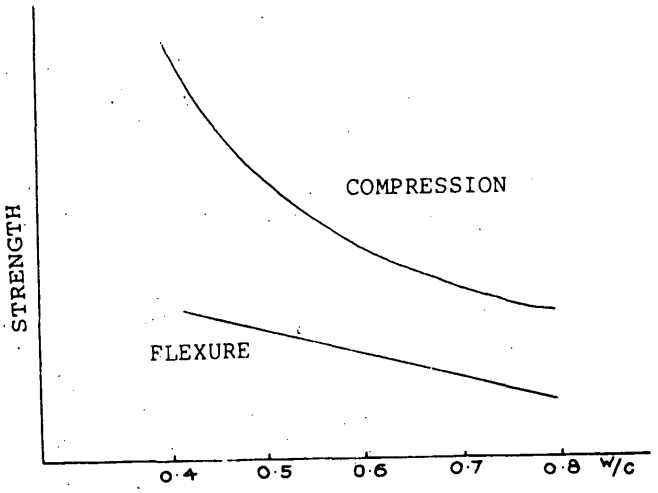


FIG. 8 EFFECT OF WATER/CEMENT RATIO ON STRENGTH

The gel/space ratio, G/S is defined as the ratio of the volume of the hydrated cement to the sum of the volume of the hydrated cement and of capillary pores. The compressive strength of concrete is observed to increase with increase in the gel/space ratio (as shown in Fig. 9).

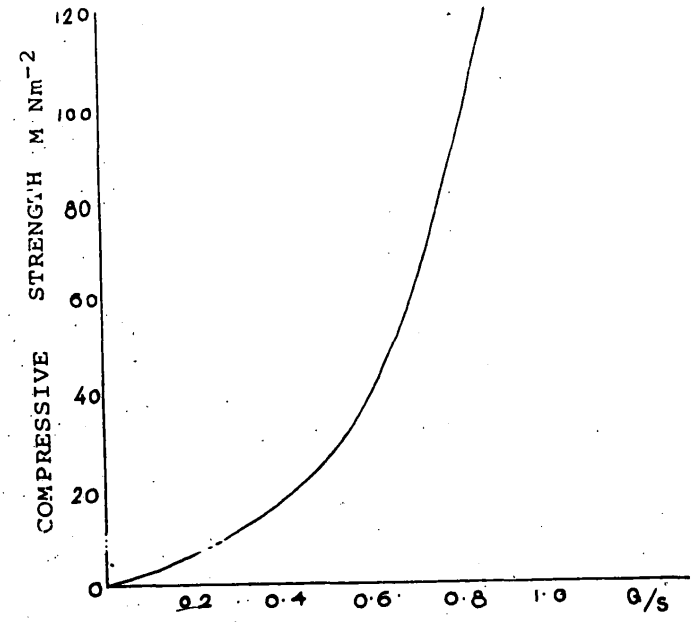


FIG. 9 EFFECT OF GEL/SPACE RATIO ON STRENGTH

Creep

Creep in concrete is unique in that it is observed only under compression, in contrast to metals which undergo creep under tension. Creep strain is of reasonable magnitude, and hence significant in the designing and construction of large structures.[25]

Creep in concrete can be identified either as basic or drying creep. When concrete is sealed to the atmosphere, and no exchange of moisture takes place with the environment it is referred to as basic creep. On the other hand, drying creep is the additional strain observed due to drying of concrete.

The mechanism of creep has not been fully understood. Many mechanisms have been proposed but each explains only a part of the observations. It is usually based on the seepage theory of concrete.[26]

On application of a compressive load in initial instantaneous deformation due to elastic responses is observed. Then the strain increases due to creep (as shown in Fig. 10).

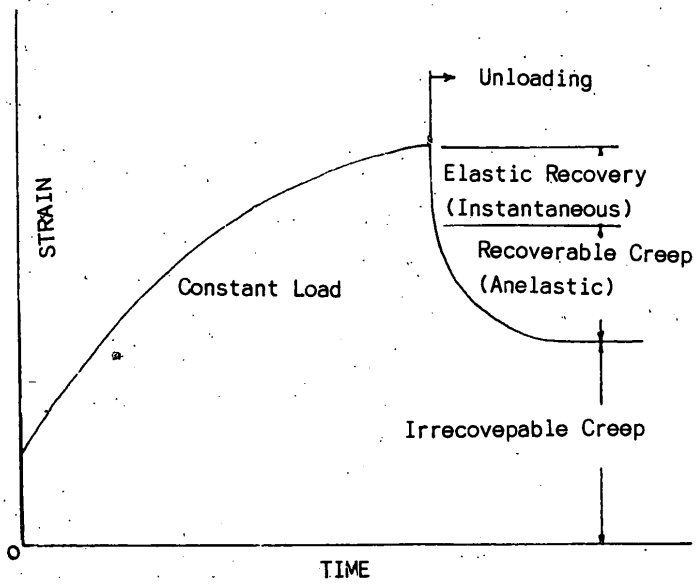


FIG. 10 LOADING CURVE ON CONCRETE

The creep mechanism is probably attributed to the movement of water trapped within the concrete. Initially the load is shared between the water and the solid material. With time, the pressurized water is squeezed out until the pressure is balanced. The load is then transferred from the liquid to the solid matrix This factor is probably responsible for the inelastic behaviour of concrete (recoverable creep). Some water may be lost to the atmosphere and this gives rise to drying creep (irrecoverable creep).[3]

The form of the creep curve given above is similar to that of a polymer. Therefore a rheological model based on a mechanical analogue has been suggested. This model cannot however explain the actual mechanism of creep in concrete.[27]

Any factor that increases the quantity of liquid and its movement is liable to affect creep. The water/cement ratio, the gel/space ratio, the richness of the mix, the quality and shape of the aggregate and cement, the temperature and the relative humidity of the surroundings and the method of curving can thus affect creep behaviour.[3]

The Importance of Structure-Property Relationships

The importance of such relationships become clearly evident if one considers the use of High Alumina Cement in structures.

High alumina cement structures widely used during World War I because of their high resistance to sulphate attack and quicker hardening characteristics than Portland cement structures were observed to fail with time. This led to the prohibition of its use in building construction. A subsequent study of the structure revealed that the initial products of hydration possess a hexagonal metastable structure which transforms with time to a more stable cubic form. This conversion it was observed was accompanied by a decrease in volume of the hydration products which increased the porosity drastically.[28, 29]

New Forms of Concrete

Concrete is a brittle material. In recent years attempts have been made to improve the properties of concrete by developing special new forms of concrete. These attempts have met with limited success.

Polymer modified concretes fall into two groups, namely polymer impregnated concretes and polymer added concretes.[30, 31]

In polymer impregnated concrete, water and air within the hardened structure is evacuated. The concrete is impreg-

nated with a liquid polymer which enters the pores and is subjected to 'in-situ' polymerization. This method of production proves to be very costly.

In polymer added concrete the polymer or monomer is added during mixing either in dispersed, granular or powder form. This type is not as expensive as polymer impregnated concrete.

Reinforced materials appear to be the material of today. The use of fibres in the reinforcement of concrete is a relatively new phenomenon. Fibre reinforcement can yield several desirable features unachievable in either of the individual components. These include high strength and toughness. The fibres used in the reinforcement of concrete include asbestos, carbon, steel, glass, polypropylene and nylon.[32 - 37]

The use of glass fibres in the reinforcement of concrete is subject to certain limitations. This is due to the susceptibility of common soda-lime glass to attack by alkali. Hence the glass fibres used in such reinforcement should be of the alkali-resistant type. Glass fibres are also subject to damage during mixing and compaction. These factors contribute to a reduction in strength.

The availability of fibres of different materials and sizes does not warrant their random use. Fibre diameter, length, orientation and the volume fraction of fibres have a significant bearing on the strength and toughness of the composite.[3] These factors should therefore be borne in mind during the production of fibre reinforced concretes.

Conclusion

Due to the presence of a number of ph in concrete, it has been difficult relate the strength to the structure, even though many attempts have been made. The structure itself needs to be better understood, to answer the fundamental question of the mechanism of failure. The influence of pore size distribution, the interconnection of pores, and the presence of interfacial cracks between aggregate and cement paste matrix on the strength should be better understood in order to propose a mechanism of failure. Once the mechanism of failure and factors which affect the strength are known, it may be possible to develop, on a scientific basis, a new type of concrete with better properties. It was shown that lack of understanding of the structure of high alumina cement concrete led to many disasters. This emphasizes the fact that it is essential to understand the structure of a new material before it is used on a wide scale.

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