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Intrinsic Instability of Hardened Portland Cement Pastes and its Significance

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Abstract: A critical evaluation of shrinkage of saturated cement paste due to thermal cycling, increased ion diffusion through saturated cement paste due to thermal cycling, Powers water permeability data of dried and resaturated cement paste, and dying shrinkage data of Pickett and others reveals an intrinsic instability of Portland cement pastes. The instability is such that even a very mild treatment of the paste causes a redistribution of pore space such that pores are narrowed in some area and widened in other areas. It is to be noted that mild drying to 94% relative humidity is sufficient to initiate this instability. These changes occur even in saturated specimens and are irreversible. These observations are inconsistent with extensive chemical bonding in hardened cement paste or the strength of chemical bonding, in cement paste, is so low that a very mild treatment can destroy them. Relevance of this redistribution to water absorption isotherms, mercury intrusion porosimetry, etc has been discussed. These techniques provide information on the treated samples and not on the microstructure of *virgin wet cement pastes* and as such they can not be used to rationalize the properties of cement pastes or concrete.

In actual use of a concrete structure, the effect of this intrinsic instability accumulates with each cycle of drying and wetting, heating and cooling etc. After a period visible, macroscopic cracks appear even in a well cured concrete structure. These macroscopic cracks are seldom healed especially within the structure where concrete is unsaturated. The accumulated effect makes the structure vulnerable to attack of all types of degrading processes like frost attack, sulphate attack, carbonation etc. These cracks may not affect the compressive load bearing capacity of a concrete structure.

Key Words: Portland cement, paste, instability, thermal cycling, diffusion, length change, shrinkage, creep.

1. INTRODUCTION

Some of the important techniques of micro-structural investigation of hardened Portland cement pastes and cement-based materials e.g. water absorption isotherms, mercury intrusion porosimetry, etc. involve sample conditioning prior to their testing. There is a general tendency to use micro-structural information i.e. the size, shape and polydispersity of the cement hydration product and their mutual geometrical arrangement, gathered from cement pastes, using these techniques, to explain properties of hardened paste or concrete or mortar. In all these, a tacit assumption is made that a matured hardened Portland cement paste has a stable structure which can withstand drying, thermal cycling, freezing, etc. without any structural change. The main object of this communication is to examine this assumption referring to the published literature. If the micro-structure changes during the sample conditioning then the relation between the micro-structure and the physical properties will be only indirect and statistical. Another object is to examine the suitability of some of these techniques for the purpose they are being used. In this examination the main emphasis is on the cement paste samples although references will also be made to Portland cement mortar or concrete specimens. In this evaluation no particular model of hardened Portland cement structure has been commented up on or emphasised. Only the general features obtained by using different techniques have been selected and critically examined. The main emphasis is on the phenomenological analyses of published experimental results and *not on any particular theory.*

2. A CRITICAL REVIEW OF THE RELEVANT LITERATURE

2.1. Instability of Cement Pastes When Cycled Through Small Temperature Range

In early 1960's Helmuth studied dimensional changes of hardened Portland cement pastes when cycled through a small temperature range [1]. For technical details Helmuth's original paper has to be consulted. To get sample uniformity, Helmuth used thin walled (approx. 7.75 mm thick), hallow cored paste samples. These pastes were cured in different ways. Those to be examined in saturated state had water on their tops straight after their casting. After 24 hours the hollow cores were also filled with water and stored at 23°C. Some pastes were cured to permit self-desiccation following a standard procedure [2]. Length of curing varied from 20 days to about 3.5 years.

After curing, one-inch (25.4 mm) long specimens were prepared from the cast samples. The length changes of these specimens were measured over a small temperature range of 2° to 25°C. However, most interesting results were obtained in the temperature range of 15° to 25°C. Fig. (**1**) shows the length change vs temperature curves of a sample which was water cured for 3.5 years. The length changes were measured whilst the specimen was in a water bath. From Fig. (**1**) it can be seen that this well cured specimen showed a permanent shrinkage of about $20x10^{-6}$ after the first cycle of cooling and

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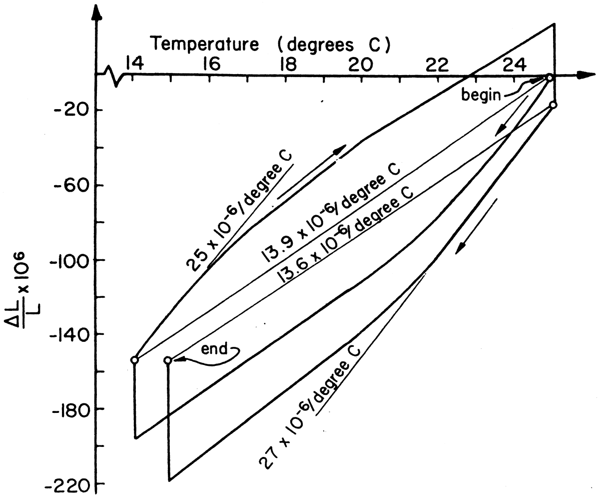

Fig. (1). Cycles of cooling and warming of 1.0 in. (25.4 mm long and 6 mm thick wall hollow cylinder) specimen in water bath. At the lowest and highest temperatures the sample was held until constant lengths were attained. Note the shrinkage at 25°C at the completion of the first cycle [1].

warming even though the sample was under water all the time. During the second cooling the specimen shrunk more than the first cooling; although the equilibrated length at 15°C was the same as in the first cooling cycle. Unfortunately, Helmuth did not continue with the second warming up; so it is not possible to state if the specimen would have increased permanent shrinkage. The permanent shrinkage at the end of the first cooling and warming cycle indicates that the specimen has altered during this cooling and warming cycle. Since the solid content of the specimen did not change this irreversible shrinkage indicates that the pore volume decreased. Recently, Scherer *et al.* also reported similar length change with warming [3]. Unfortunately, however, Scherer *et al.* did not cool their specimens to the starting temperature so any possible permanent shrinkage was not observed.

Fig. (**2**) shows three cycles of the length change vs temperature change curves of a self-desiccated specimen. The pores were calculated to be 82% water filled and the internal relative humidity of the samples was 94%. During this experiment the specimen was immersed in mercury. It can be seen that at the end of each cycle of cooling and warming the specimen showed progressive permanent expansion. This progressive expansion is reminiscent of formation of cracks and their extension in some consolidated materials e.g. glaze on ceramic bodies. Since the total material remained essentially constant this permanent expansion shows that the pore volume, if not the structure, was expanding.

From Figs. (**1**) and (**2**) one may conclude that matured cement paste, when cycled through 10°C temperature range, may shrink or expand depending on its state of water saturation. A fully saturated specimen shrinks and a self-desiccated specimen expands. In either case cement paste shows intrinsic volume instability resulting from its micro-structural instability (see also the following sections). It is of interest to note that mild drying only to 94% relative humidity is sufficient to initiate this instability.

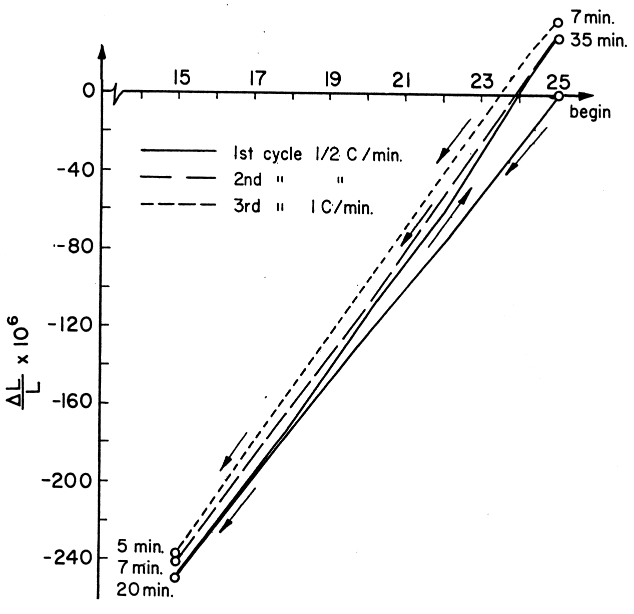

Fig. (2). Cycles of cooling and warming of 1,0in. (25.4 x 25.4 mm solid cylinder) self-desiccated specimen immersed in mercury. Note the increase in lengths of the specimen after each complete cycle. At the lowest and highest temperatures the sample was held until constant lengths were attained [1].

2.2. Increased Ionic Migration Through Thermally Cycled Cement Pastes

Diffusion of ions through a cement paste is very sensitive to any alteration in the internal structure of a cement paste. Atkinson and Nickerson measured radio active I^- ion diffusivity in the same specimen (specimen size was 32 mm diameter, 3mm thickness) as a function of temperature cycle from 20°C up to 60°C, down to 10°C and then back to 20°C. The results clearly demonstrate that these temperature changes have an irreversible effect on the structure in such a way as to increase the diffusion coefficient. An increased diffusion coefficient means either the channels, through which diffusion occurs, have increased in size or shortened in length. From other related work the authors concluded, "These data confirms that irreversible changes are induced by the thermal cycles." [4]. In all these experiments the samples were all the time under water. From Helmuth's results [1] on saturated samples one would expect that Atkinson and Nickerson's samples to shrink. Since solid materials of the specimen remained unaltered, the expected volume shrinkage should have increased the density of these samples and decreased ionic diffusivity through them. The observed increased diffusivity then indicates that some of the diffusion channels became wider and/or shorter to cause this increase and other channels have collapsed to the extent that the samples shrank.

2.3. Increased Hydraulic Permeability of Slowly Dried and Resaturated Cement Pastes

This aspect was studied by Powers *et al.* [5]. These authors slowly dried cement paste specimens, in two stages, to 79% relative humidity. Then they slowly resaturated the specimens to 97% saturation. By this procedure the moisture changes occurred slowly, and the stresses arising from differential shrinking or swelling were correspondingly low. Hydraulic permeability were measured on these specimens and compared to companion virgin specimens. “Gradual drying to 79% relative humidity increased the coefficients of permeability about *seventy-fold*.” (emphasis added by SC). The authors explained the observed increase in the permeability coefficient to rapture of some of the webs of gel between capillary cavities.

Subsequently, this data was further analysed by Chatterji [6]. That analysis showed that either the transport channels, through which water was being transported, were shortened by a factor of 70 or out of original 8 water transport channels 7 had irreversibly collapsed making the last one correspondingly larger or a combination of these two modes must have occurred during drying and resaturation. In either case the original internal paste structure had been drastically altered.

2.4. Drying Shrinkage of Cement-Based Materials

A cement-based material when dried undergoes volume shrinkage. The drying shrinkage of a concrete mix decreases with increasing aggregate content. Pickett studied this aspect both experimentally and theoretically [7]. 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 a concrete containing that cement:

$$S_c = S_p (1-V_a)^n \text{ ....} (1)$$

where S_c is the shrinkage of concrete,

S_p is the shrinkage of cement paste,

V_a is the fractional volume of aggregate,

n is a constant.

Pickett's own results yielded a value of n as 1.7, although values from 1.2 to 1.7 have been reported by other workers [8].

It is of interest to examine equation (1) closely. The volume content of cement paste of most usual concrete is about 30% and that of aggregate is about 70%. In most concrete samples the aggregates tend to have better elastic properties than the cement paste. From equation (1) it can be calculated that in the concrete a fraction of its paste content, between 0.236 and 0.129 depending on the value of n, effectively contributes to the concrete shrinkage. In other words between 21 and 57 % of the paste content i.e. on the average about 40%, has zero effective shrinkage. *Perhaps more realistically whole of cement paste in concrete specimen has been changed such that it has an effective drying shrinkage of about 60% of unadulterated cement paste.* Winslow and Liu [9] have also concluded that the presence of the aggregate particles alters the structure of cement paste considerably. (See also Chatterji [10]).

3. DISCUSSION OF THE ABOVE RESULTS

3.1. Small-Angle X-ray Scattering by Hydrated Portland Cement

As a preliminary to a discussion of the above results of different workers, it is in order to examine the small-angle X-ray scattering by hydrated cements. This technique has certain advantages over other techniques discussed so far.

X-ray photon are scattered whenever they pass through regions of differing electron density either within a material or at the interfaces of a material of one electron density and surrounding phase of a different electron density. This second type of interfacial scattering is diffuse and occurs at small-angle. With certain assumptions, Porod related the shape of the small-angle scattered intensity curve to the specific surface area of an assembly of colloid sized particles [11]. Porod showed that a particular function of the small-angle scattered intensity when plotted against increasing angle asymptotically approaches a limiting value. This limiting value is proportional to the specific surface area of the particle assembly. *Most interestingly, the shape of the above asymptotic curve can be determined experimentally without any assumption.* If a chemical or physical treatment alters the characteristics of the particle assembly by altering the average size of the assembly or its polydispersity then the shape of the asymptotic curve also changes. With this change in the shape of the curve the calculated specific surface area of the assembly of particles also changes irrespective of the of validity Porod’s assumptions. Thus a comparison of the calculated specific surface areas of a treated assembly with that of the untreated sample can be used directly to monitor the affect of the treatment without any assumption. *Thus the changes in average size of the scattering particles or its polydispersity could be followed.* These are the main advantages of the small angle X-ray scattering technique.

Winslow and Diamond studied a series of Portland cement pastes, hydrated to 86% at a w/c ratio of 0.4 by small-angle X-ray scattering technique [12]. These authors dried the hydrated paste to different stages, examined the dried samples, then resaturated the dried samples and examined again. Table **1** shows a summery of the results. These results show that all dried samples have lower specific surfaces area than the virgin sample. After resaturation most of the dried samples regained their original specific surfaces area i.e. the size and polydispersity of the primary particles remained unaltered. The probable exceptions are those dried at 105°C. In these cases net surface losses are about 7%. These results show that hydrated samples suffered *no permanent alteration either in the average size or in polydispersity* by both P- and D-drying; samples regained their original specific surface on resaturation. Even drying at 105℃ caused only a minor permanent change. With these results, different works referred to in section **2** could be analysed.

The physical meaning of this loss of specific surface area due to drying is not clear although various suggestions have been made. Phenomenologically, this loss of specific surface area indicates an agglomeration of primary particles (of cement hydration products) in such a fashion that small-angle X-ray scattering could not distinguish the primary particles in the agglomerates. However, the primary particles did not loose their identity. On resaturation, the primary particles regained their original specific surface area. Notice that the ratio of specific surface areas of a dried sample and the corresponding saturated sample varies with the method of drying. These ratios are not simple fractions.

Table 1. Surface Areas of 86% Hydrated Portland Cement Pastes at w/c of 0.4

State of the Sample	Surface area (m^2/g ignited at 1050 °C)	
	After Treatment	After Resaturation
	Average of 3 Replicates	Average of 3 Replicates
Saturated	708	
Dried at 52% r.h.	330	
P-dried[1]	272	697
D-dried[2]	224	707
Oven dried at 105℃	180	651
Vacuum-oven dried at 105℃	138	655

[1]) Cement powder dried, under vacuum, over a mixture of Mg $(ClO_4)_2.2H_2O$ and Mg $(ClO_4)_2.4H_2O$.

[2]) Cement powder dried, under vacuum, to equilibrium on ice at dry ice temperature.

3.2. Effects of Thermal Cycling Through Narrow Temperature Range on the Structure of Cement Paste

The samples of both Helmuth and Atkinson and Nickerson have remained saturated throughout the experiments. Small-angle X-ray scattering results indicates that the particles of cement hydration products did not suffer any alteration in size or polydispersity (see **3.1**) and observed changes are therefore external to the geometry of the hydration products i.e. hydrated particles. The results of Helmuth and those of Atkinson and Nickerson, both on saturated specimens, when considered together indicate that cycling though comparatively small temperature range alters the relative arrangements of the primary hydrated particles This happens in spite of the specimens remaining under water all though the experimentations i.e. without surface tension of water playing Items **3.2** and **3.3** any part. These are surprising results. Irreversible shrinkage in Helmuth's results indicates that the pore volume has decreased due to the temperature cycling. Increased diffusivity of I^- ion in Atkinson and Nickerson's experiments indicate that some of the diffusion channels have collapsed whilst others have increased in widths and/or the path lengths of diffusion have decreased. Together, the above results indicate that whilst the total pore volume is decreasing their widths are increasing or lengths are decreasing i.e. the structure of the paste changed i.e. the structure is intrinsically unstable. (See also the section **3.3**).

Chemically bonded porous materials e.g. porous metal plates, porous glasses etc do not show above types of instability i.e. strength of bonding is strong enough to withstand above types of treatment. The behaviours of cement pastes are inconsistent with extensive chemical bonding in hardened cement paste or the strength of chemical bonding in cement pastes is so low, compared to chemically bound porous glass etc, that a very mild treatment (for example drying to 94% relative humidity) of the specimens could destroy them irreversibly. However, physical bonding allows for easy rearrangement of hydration products in a hardened paste. For example physically bonded marbles expand when thermally cycled whilst submerged under water [13].

3.3. Effect of Mild Drying on the Structure of Cement Paste

From Powers *et al's* observation on water permeability one would conclude that drastic, irreversible alteration of paste structure occurred during drying to 79% relative humidity. Combining, Helmuth's observations on self-desiccated pastes and Powers *et al's* observation on water permeability one would conclude that drastic, irreversible alteration of paste structure starts at relative humidity of 94% or higher. These results also point to uneven changes in pore structure. Powers *et al's* results show that these changes could not be reversed by saturating with water.

3.4. Effects on Individual Hydration Products

Items **3.2** and **3.3** only refer to arrangement of hydration products and strength of their mutual bonding but give no information about individual hydration products; their sizes, shape or relative arrangement.

3.5. Assumed Relationship Between Neat Cement Paste and Cement-Based Materials

Drying shrinkage results of Pickett and others also indicate that drying causes alteration of paste structure of the whole specimen. It is also obvious that the behaviour of neat cement paste is very different from that in concrete or mortar.

4. SOME IMPLICATIONS OF THE ABOVE RESULTS ON EXPERIMENTAL TECHNIQUES USED FOR MICRO-STRUCTURAL INVESTIGATION OF HARDENED PORTLAND CEMENT PASTES AND CEMENT-BASED MATERIALS

4.1. Mercury Intrusion Porosimetry (MIP)

This technique is used to measure the total porosity and pore-size distribution in cement pastes. Often the results of these measurements are used to explain properties like frost resistance, chemical attack etc. of concrete or mortar. For this technique, the specimen has to be dried to remove all traces of water in pores. Normally a specimen is dried under vacuum at an elevated temperature. This pre-treatment of a specimen alters both the total pore volume, and the pore size distribution of the specimen. The small-angle X-ray scattering shows that the hydration products loose a part of their specific surface area during drying i.e. the primary hydrated particles form agglomerates. Powers has already reported an irreversible volume reduction of about 4% due to drying even though his paste samples were crushed to 48-100 mesh size prior to drying [14]. Powers' water permeability results and those of Helmuth and Atkinson and Nickerson indicate that pore size distribution is also altered. All these mean that MIP results refer to the characteristics of dried specimens and these results can not be referred to their companion virgin specimens. Attempted explanation of physical properties like frost resistance or chemical attack on the basis of the MIP results may not be appropriate.

4.2. Techniques of Water Vapour Adsorption and Related Changes in the Properties of Cement Paste

Like the MIP technique, these also require extreme drying of the test specimens prior to their exposure to water vapour at different relative humidity. The drying technique varied from equilibrating the specimens to very low relativity humidity at the room temperature to vacuum degassing at 80° or 96°C. The extensive literature, up to 1980, has been reviewed by Ramachandran, Feldman and Beaudoin [15]. These authors, themselves contributed much to the development of these techniques. These authors made a singularly important statement "Thus, the structural nature of the specimen in the virgin wet state cannot be ascertained." [16]. By the authors' own admission the results of this technique has no relevance to untreated sample. One has also to consider the effect of crack formation in paste specimens due to severe drying and loss of coherence of the specimens [17]. Ramachandran *et al.* did not take into account of these crack formation in their specimens.

4.3. Irreversible and Reversible Shrinkage of Cement Pastes

On drying for the first time, a paste specimen undergoes volume shrinkage. On re-saturating only a part of the initial shrinkage is recovered and the rest is permanently lost. In subsequent drying-wetting cycles, the volume of the specimen oscillates nearly reversibly but not precisely.

Now consider a hardened cement paste specimen which was kept under water from the very beginning. In this specimen individual particles of the specimen are separated from their immediate neighbours by water layers of varying thickness. On first drying these inter-particle water layers evaporate bringing the particles near to each other and causing volume shrinkage. Only a part of the total volume shrinkage appears as external volume shrinkage; the other part is lost internally (see **2.3** and **3.3**). On re-saturating, individual particles regain a layer of water corresponding to the ambient relative humidity and no more. These adsorbed water layers separate the neighbouring particles by, at most, twice the thickness of the adsorbed water layer. That means the water layers will have a definite thickness. There is no force to cause higher separation. The differences between the thicknesses of the initial water layers and the adsorbed water layers appear as the irreversible shrinkage. In subsequent drying-wetting cycles the thickness of the adsorbed water layers oscillates between drying and wetting limits. The specimen then shows near reversible drying shrinkage.

However, in the absence of extensive inter-particle strong chemical bonding, as is evident from Helmuth and Atkinson and Nickerson's results, the particles are still free to arrange themselves in subsequent drying-wetting cycles. This rearrangement shows up as small, continued deviance from reversible drying shrinkage.

From the results of Helmuth and Atkinson and Nickerson and Powers' *et al's* water permeability tests it can be seen that the volume distribution of the solid particles is not uniform over a specimen. Under certain circumstances this non-uniform distribution may show up as micro-and macro-cracks. In this case, reversible and irreversible shrinkages loose all meanings. Visual evidence of crack formation in drying paste specimen of less than 1mm thickness has earlier been presented [17]. Continuum mechanics can not be used to relate the microstructure of a cracked specimen to its macro-properties. The continuum mechanics can still be used to study macro-properties on the assumption of a representative volume containing all the alterations. However, that procedure does not relate micro-structure to the physical properties of hardened cement paste.

4.4. Microstructure of Cement Paste and Drying Shrinkage and Creep of Concrete

Unlike cement paste specimens, concrete specimens are massive. Their bulk brings some other factors in to play. In a theoretical paper it has been shown that a under water stored concrete specimen of usual dimension (say 10x20 cms cylinder) has a thin outer rim which is saturated and bulk of the rest remains unsaturated [18]. Best experimental evidence for this has been reported by Collepardi [19]. Collepardi subjected concrete cylinders (10x20 cms), after water curing for different periods, to ISO-7031 test. In this test method concrete cylinders are subjected to water pressure up to 7 bars. Collepardi's results show that bulk of all concrete cylinders, with water/cement ratio of 0.55 or below, are unsaturated after 28 days water curing. Less than 20 mm of outer surface is saturated at the end of the specified pressure treatment.

The above state of affair makes theoretical analyses of drying shrinkage and creep of concrete structure hazardous. Consider a fully saturated concrete specimen under hydrostatic compression. No creep can occur except for a very small decrease in total volume due to the compression of solid and water. On the removal of compression the volume is fully recovered. If the specimen is partially saturated, as most concrete specimens are, then compression stress is carried *mainly* by the solid components as water flows to the unoccupied sites. Volume decrease i.e. creep is due to the compression of the porous solid body. This water flow is a slow process as it flows through narrow channels. The accompanying volume decrease i.e. creep is also a slow process. On removal of compression only the part of water still under compression returns to the original sites. However, the part of water which has moved to originally unoccupied sites will not return back to their original sites. Thus the creep recovery can only be partial i.e. there will be an irreversible creep. In addition, a part of solid, as the results of Helmuth and Atkinson and Nickerson show, also moves and fills a part of the original unoccupied sites thus contributing to the total irreversible creep.

4.5. Hydraulic Permeability of Concrete and Cement Paste

Results of Helmuth and Atkinson and Nickerson suggest that hydraulic permeability of virgin cement paste and concrete will also increase if these materials are cycled through a narrow temperature range. However, no experimental evidence has been reported.

CONCLUDING REMARKS

The microstructure of hardened Portland cement paste and cement based materials is intrinsically unstable. This instability shows up as altered pore structure in fully saturated paste during thermal cycling, in partially died and re-saturated paste and drying concrete. The total porosity alters in such a fashion that some of the pores decrease in volume and some others increase in volume. In extreme cases the alteration could lead to micro-and macro-cracks. Other significances of this structural alteration have been discussed. The main point is that many of the techniques used to infer the virgin microstructure of cement-based materials give information of altered specimens (see comment by Ramachandran *et al.* in the section **4.2**).

In a concrete structure in use, the effect of this intrinsic instability increases with each cycle of drying and wetting, heating and cooling etc. Over a period macroscopic cracks form even in a well made concrete structure. These macroscopic cracks are seldom healed especially within the structure where concrete is unsaturated. The accumulated effects makes the structure vulnerable to attack of all types of degrading processes like frost attack, chemical attack, reinforcement corrosion etc. Notice that in a well made and well cured concrete structure visible cracks appear only after a period of use.

It has also to be remembered that in a structure concrete is designed to carry the compressive load. The compressive strength of a brittle material is a function of shear strength and is not sensitive to micro- and macro-cracks. A concrete structure can take lots of insult before its compressive load bearing capacity is affected. However, under proper conditions cracks may reach the reinforcements and start reinforcement corrosion i.e. the service life would be impaired. Other similar conditions could easily be imagined. The object of this last paragraph is to assure the practicing concrete technologists not to panic but to be careful in designing a structure and proper maintenance.

A reviewer has raised the point whether prolonged underwater storage will self-heal the instability developed during cycling as discussed above. This is a question needs specific research project to settle. However, the bulk of mass concrete structures remain unsaturated even when stored underwater. The present author has noted unsaturation in the underwater section of a jetty after 4 years of use (see also [19]). One would not expect much self-healing under this condition.

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