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MECHANISM OF EXPANSION OF CONCRETE DUE TO THE PRESENCE OF DEAD-BURNT CaO AND MgO.

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ABSTRACT
A new mechanism has been proposed to explain the delayed expansions, due to the presence of dead-burnt CaO or MgO, of Portland cement based materials. The mechanism is based on the crystal growth pressure, the solubility of hydroxide crystals, their growth habits and diffusion of Ca^{2+} and Mg^{2+} through the electrical double layer which forms round cement hydration products. In this mechanism the crystal growth pressure is the expanding agent and the others are modifiers.

Introduction

For the long term stability of a cement based structure, it is important that the cementitious material shall not undergo any appreciable volume change over and above that associated with the moisture movement. However, nearly from the very inception of Portland cement manufacture, it was observed that the presence of uncombined CaO in the final product causes excessive expansion after some delay. That the presence of uncombined MgO also causes delayed excessive expansion was first noticed in 1884, first in France then in Germany.

The expansion of a cement based materials, containing free CaO or MgO, is due to the delayed hydration of these two oxides. At the clinkering temperature of about 1400°C free CaO or MgO are in a dead-burnt state. Under the usual conditions of use of cement either of these dead-burnt oxides may take considerable time before they hydrate. These oxides are often enclosed within other clinker phases which also delay their hydration. Of the two oxides, CaO is intrinsically more reactive than MgO and its hydration product i.e. $Ca(OH)_2$ is more soluble than $Mg(OH)_2$. This association of paste expansion with the formation of $Ca(OH)_2$ or $Mg(OH)_2$ from their oxides led to the corresponding test methods of monitoring the volume increase during boiling in water of a preshaped cement paste (Le Chatelier test) for CaO and autoclaving of cement paste prism at 216°C for MgO and CaO.

In spite of a large volume of work on the subject the mechanisms of these volume expansions are not well-understood. The object of this paper is propose a mechanism to explain these expansions.

Some empirical observations.

In order to understand the probable mechanisms of these expansions it is necessary to be acquainted with some empirical observations.

i) A molar solid volume expansion of about 90% occurs during hydration of CaO to $Ca(OH)_2$ and for MgO the increase is about 117%. If this molar volume increase was the main cause of expansion then more expansion would have been expected in the case of MgO than CaO. Whereas storage of neat paste and mortar bars in water and autoclave expansion measurements of neat paste bars showed that about 1.4-2% CaO and about 4-5% MgO is needed to cause any excessive expansion (1,2). This difference in the expansion capacities could not be accounted for by the molar solid volume expansion i.e. the solid state hydration of the oxides and needs some other explanation.

ii) Air-stored neat paste bars made with high CaO cements first contract and then expand and in some cases expansions are more than the companion bars stored in water. However no such reversal of the expansion characteristics occurs with mortar prisms made with those cements irrespective of the storage conditions. (1).

iii) The autoclave expansion tests of cements of varying MgO or CaO contents show that the expansion increases sharply above a critical value of MgO or CaO. However no such critical value was observed in cases of bars, neat paste or mortar, during 10 years storage in water (1).

iv) Various authors have shown that for a given content of MgO the autoclave expansion increases sharply with increasing particle size of MgO (1,3,4). Keil found that 4% MgO below 5μm size produces about the same autoclave expansion as 1% MgO of 30-60μm size (3). This large variation in the expansion capacity with particle size could not be explained by the quicker hydration of small MgO particles as similar differences in the expansion capacity between 15-30μm and 30-60μm sizes has also been reported (4). A similar decrease in the autoclave expansion capacities of cements has been observed for quickly cooled clinkers compared to slowly cooled clinker. Microscopic and other investigations showed that the size of MgO particles were smaller in quickly cooled clinkers compared to slowly cooled clinkers (1).

v) Ramachandran et al have studied the expansion and hydration processes of compacts of CaO both in the presence of water vapour and liquid water (5). In both the cases compacts contained 54 volume % CaO and 46 volume % void. The compacts, which were hydrated in the presence of liquid water, expanded by 23% by volume; at the same time its void was reduced form 46% to 16%. Thus in the liquid hydration void was decreased. In contrast to above, the vapour phase hydration of the compacts showed that there was a volume increase to 400% by the time all CaO had hydrated. The expansion continued, with scarce slow down, to 600%. After this large expansion the rate slowed down and beyond 800% expansion the compacts gradually disintegrated.

Mechanism of expansion.

All the above observations can be given a self-consistent and coherent explanation on the basis of crystal growth pressure, the solubilities of hydroxide crystals, their growth habits and diffusion of Ca^{2+} and Mg^{2+} through electrical double layer which forms round cement hydration products. However it will be useful to start with the hydration of neat CaO compacts.

a) Expansion of CaO compacts.

The contrasting observations of liquid and vapour phase hydration could be explained in terms of crystal growth pressure, the elongated growth habit of $Ca(OH)_2$, and the differences in the diffusivity of Ca^{2+} and OH^- through water filled pores and surface layers.

Hydration of CaO, irrespective of hydration environments, initially forms very fine calcium hydroxide crystals between 10 and 20 nanometres in size (6). These small crystals subsequently recrystallize into comparatively large and elongated micrometer sized crystals (6,7). Initially formed fine crystals have higher solubility than larger crystals. A solution in contact with a mixture of fine and large crystals is supersaturated with respect to the larger crystals. In this condition the larger crystals grow in size at the expense of the fine crystals and if restrained develop an outward thrusting pressure on the restrains. This excess pressure, *on the constraint*, is known as the crystal growth pressure. The crystal growth pressure, ΔP, is given by

$$\Delta P=\frac{RT}{V_M}\ln\frac{a_s}{a_0}\ldots\ldots\ldots\ldots[1]$$

where V_M is the molar volume of the crystal; a_s is the mean activity of the supersaturated solution; a_0 is the mean 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 (8).

The difference in the expansion capacities of liquid and vapour phase hydration of CaO could be explained as follows. In the liquid state hydration, the initially formed, very fine $Ca(OH)_2$ crystals are dispersed within the pores of the compact. Due to the higher diffusivity of Ca^{2+} and OH^- ions in the presence of liquid water, present in the compact, the supersaturation of the liquid phase tends to be the same all over the compact. In this circumstance, the nuclei which are not under any constraint, i.e. which are adjacent to or in the voids, will grow more than those that are under constraint. Because of this crystal growth at preferred places, the voids will be filled up without causing much expansion as has been found by Ramachandran et al (5).

In the vapour-phase hydration, on the other hand, the very fine crystals of $Ca(OH)_2$, due to the absence of liquid water, are not dispersed throughout the compact and remains at or near their sites of formation. The fine crystals adsorb water on their surface forming a layer but not necessarily a continuous layer. In this case, only short-range diffusion of Ca^{2+} and OH^- ions, through the overlapping water layers can occur; but not the long-range diffusion which is possible only in completely water-filled compacts. Due to this short-range diffusion the crystal growth is localized. This localized anisotropic crystal growth develops the crystal growth pressure on the contacting particles, and thereby creating and /or expanding the volume of voids in the compacts as has been observed by Ramachandran et al in their vapour phase hydration. As fine crystals of $Ca(OH)_2$ are available even at the complete hydration of CaO, the expansion of the compact continues until the fine crystals are completely consumed.

b) Expansion of cement based materials.

The above mechanism can be extended to Portland cement based materials. In the case of a cement based material unhydrated CaO or MgO particles are embedded in the set cement. This embedding delays the rate of hydration of the oxide particles, prevents any dispersal of hydroxide particles and forces crystal growth to occur locally. As a result of the slow rate of hydration of oxide particles the volume of fine grained hydroxide particle, at any given time, is limited. This limited supply of fine grained hydroxide crystals limits, at the time, the volume of the large, elongated crystals, the effective agents for the transference of the crystal growth pressure to the surrounding matrix and expansion (8).

The embedding, on the other hand, keeps all the initially formed fine hydroxide crystals together thereby opening the possibility of growth of a larger volume of elongated crystals than if the initially formed hydroxide crystals could be dispersed. The larger the original oxide particle the larger is the volume of enclosed fine hydroxide crystals and higher is the volume of possible elongated crystal growth and so also the expansion capacity. This explains the effect of particle size of oxide particles on the delayed expansion.

The surrounding cement paste is partly or fully saturated with an alkaline solution. This solution allows for the diffusion of Ca^{2+} or Mg^{2+} and OH^- ions out of the supersaturated solution which surrounds the hydrating CaO or MgO particles. The effective supersaturation will be the net result of the solubility of fine hydroxide crystals and the above diffusion. The effective supersaturation will always be lower than that expected from the size of fine hydroxide crystals. The reduced effective supersaturation reduces the crystal growth pressure. The slower the rate of oxide hydration more will be the diffusion and the lower will be the effective supersaturation, the crystal growth pressure and hence the lower expansion. This partly accounts for the lower expansion capacity of slowly hydrating MgO compared to CaO.

There is a modifying factor which affects the above ion diffusion.

The diffusion of positive ions occurs mainly through the electrical double layer. This double layer has a high concentration of divalent positive ions e.g. Ca^{2+} or Mg^{2+} (9). In normal Portland cement paste Ca^{2+} is the main divalent positive ion in the double layer. This high concentration of Ca^{2+} in the double layer in the paste matrix restricts the diffusion of Ca^{2+} ions away from the surrounding of hydrating CaO particles i.e. the effective supersaturation round the hydrating CaO particles is higher. In the near absence of Mg^{2+} ions in the double layer in the paste matrix the diffusion of Mg^{2+} ions from the hydrating MgO particles is unhindered. This lowers the local effective supersaturation of $Mg(OH)_2$ and its expansion capacity compared to CaO. This is another contributing factor in the lower expansion capacity of MgO compared to CaO.

It is now possible to explain the empirical observations listed above. The difference between the air stored and water stored neat cement bars of high free CaO cements could be explained as due to the lower diffusion of Ca^{2+} and OH^- ions in the partly dried air stored bars. Whereas the diffusion of ions is higher in the saturated water stored bars both of neat paste and mortar and hence lower supersaturation and lower expansion. The initial shrinkage of the air-stored bars may be attributed to the initial drying.

The sharp rise of autoclave expansion in cement pastes when the content of free CaO or MgO is above the critical values could be explained as follows. During the autoclaving of the neat cement bars both the hydration of free oxide and the elongated growth of hydroxide occur simultaneously and quickly. There is no time for diffusion of ions and the lowering of supersaturation. This causes the sharp rise in expansion in the autoclave tests. In the case of water storage, the free oxide particles hydrate slowly and there is the time for the diffusion of ions away from the hydrating oxide particles. This diffusion of materials not only reduces the supersaturation but also removes Ca^{2+}, Mg^{2+} and OH^- ions from the neighbourhood of the hydrating oxide particles thereby reducing the material source for elongated growth. The net result is a slow rise of expansion of water stored bars with the free oxide content of the cement (1). It is also observed that the rate of increase of expansion with MgO content is some what higher in neat cement bars than in mortar bars made with same cements (1). This last observation can also be ascribe to the higher possibility of diffusion in the case of mortar bars.

It will be of interest to calculate the approximate degree of supersaturation that is needed to overcome the tensile strength of concrete and cause expansion. A good quality concrete will have a tensile strength of about 3 MPa. For this estimation [1] could be modified by using the concentrations C's instead of the activities a's. The molar weight and density of $Ca(OH)_2$ are 74 and 2230 kg/m^3 respectively; the corresponding values for $Mg(OH)_2$ are 58.3 and 2368 kg/m^3. At 25°C the calculated C_s/C_0 ratios are 1.04 for $Ca(OH)_2$ and 1.03 for $Mg(OH)_2$ i.e. the values are of the order of magnitude that may be expected from the presence of fine grained hydroxide crystals. From the Kelvin's equation, relating solubility with the particle size, it may be estimated that in the colloid range a size ratio of about 30 between the smallest and the largest crystals will be sufficient to develop the required supersaturation. Actually the observed size range varies from about 10 nanometres to a few microns i.e. much more than is required to develop the required supersaturation (6).

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