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The volume expansion of hardened cement paste due to the presence of “dead-burnt” CaO*

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Dr Chatterji and Dr Jeffery have produced some interesting results on hydration of CaO in liquid water and the associated ageing of the product, although much work^(1,2) has already been published on various aspects of ageing (decrease in surface area and increase in crystal size). This paper, however, presents no new evidence concerning the mechanism of hydration in the presence of water vapour.

We attempted, in the paper⁽³⁾ to which the authors refer, to explain the differences of the hydration process of CaO, as performed by water in the vapour and in the liquid phase. Vapour-phase hydration produced the abnormally high volume expansion to which the authors refer; liquid-phase hydration produced a linear expansion of 8%. The authors, however, relate the results of their liquid-phase experiments to those we obtained from vapour-phase experiments.

In discussing the possibility of topochemical reaction, the authors assume that a crystal of CaO would be required to transform as a block to Ca(OH)_2 . This is not necessarily correct. Our experiments⁽³⁾ showed that hydration by vapour produces a high-surface-area product suggesting that, as the reaction proceeds at the surface, the product breaks away into fragments. Hydration of CaO can occur rapidly at relative pressures of water vapour at which one would expect less than a monolayer because of the physical forces of adsorption alone.

The authors imply that particles of CaO in a compact are not restrained. This is not correct because a compacted specimen of CaO has strength and a measurable value of Young's modulus. Hydration by vapour, however, produces a very weak body which

gradually disintegrates into a fine powder and this result supports the idea that the reaction is occurring at the surface without much of the recrystallization and regellation that occurs during solution reactions. The 40% expansion after completion of hydration may be also due to simple gravity flow of a loose powder unable to retain its shape when all the bonds of the compact have been broken. The compact was positioned horizontally and measured along the diameter.

In contrast to the above result, our experiments involving hydration of CaO compacts in liquid water show that this reaction results in a relatively low expansion of the compact and a decrease in porosity, and is accompanied by the formation of a strong body. This is consistent with a solution mechanism in which crystallites are forming and growing throughout the pores cementing the system together.

We wish to restate that our experiments have shown there are two mechanisms for hydration of CaO—one primarily a solution mechanism and the other a topochemical reaction at the solid-vapour interface. Chatterji and Jeffery confirm the first mechanism but in no way show any evidence to discount the second mechanism as postulated by us.

Reply by the authors

THE POSSIBILITY OF TOPOCHEMICAL REACTION

In a topochemical reaction the maximum expansion that can occur in a single crystal equals the volume difference between the reaction product(s) and one of the reactants; in this case CaO. We agree with Ramachandran et al. that it is not necessary to assume that a crystal of CaO will transform as a block to Ca(OH)_2 ; in fact, in our mechanism we have not

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assumed it. But if we assume that the hydration product "breaks away into fragments", the expansion should be less than the theoretical one. Let us take a crystal of CaO which has a void on one side but is surrounded on its other sides by particles of CaO. The hydration products which are forming on the grain boundaries will push apart the grains in contact, but the reaction products forming on the void side will break away and fill the void without causing any expansion. Thus we cannot expect even the theoretical expansion in a CaO block containing voids, let alone an expansion beyond the theoretical value as found by Ramachandran et al. The very fact that they got more than the theoretical expansion with their blocks containing 46% voids in itself suggests that some processes other than simple solid-state reaction were operative in their experiments in the vapour state. Moreover the topochemical reaction mechanism cannot explain the 40% expansion which took place after complete hydration of CaO.

THE EXPANSION AFTER COMPLETE HYDRATION OF CaO

To explain the 40% expansion after complete hydration, Ramachandran et al. originally suggested an 'ageing effect'. They now appear to have abandoned this explanation and have suggested that it may be "due to simple gravity flow of a loose powder unable to retain its shape . . .". In terms of volume change, the 100 cm³ of compacted calcium oxide, which has become 408 cm³ after 50 h, increases to about 600 cm³ by 75 h and the rate of volume expansion has scarcely slowed down from that at 50 h (when all CaO is hydrated). Beyond 200 h (when the volume has become 800 cm³) "the compact gradually disintegrates"⁽³⁾. This can only mean that it has retained its shape up to this point. It is thus difficult to see how 'gravity flow' can account for the 200 cm³ expansion between 50 and 75 h, long before any signs of disintegration become apparent.

THE RELATION BETWEEN VAPOUR AND LIQUID HYDRATION OF COMPACTS

Ramachandran et al. have found that, in liquid hydration, a 100 cm³ compact of CaO (containing 54% CaO and 46% void) expanded to 123 cm³ in which 107 cm³ was occupied by Ca(OH)₂ and 16 cm³ by the voids. Thus the formation of Ca(OH)₂ had decreased the amount of voids. In contrast to this, in vapour-state hydration, a 100 cm³ compact of CaO, of the above-mentioned characteristics, expanded to 408 cm³, in which 107 cm³ was occupied by Ca(OH)₂ and 301 cm³ by void.

Now let us see how these striking differences can be explained by our proposed mechanism. In the liquid hydration, the initially formed, very fine Ca(OH)₂ crystals will be able to disperse throughout the block owing to the lubricating action of the liquid water and

the brownian motion of the crystals. Owing to the higher diffusivity of Ca and OH ions in the presence of liquid water, the concentration of Ca(OH)₂ in the liquid phase will tend to be the same all over the block. In these circumstances, 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 without causing much expansion, as has been found by Ramachandran et al.

In the vapour-state hydration, on the other hand, the very fine Ca(OH)₂ crystals will not be dispersed throughout the block because of the lack of lubricating liquid. These fine Ca(OH)₂ crystals will adsorb a layer of water vapour, but not necessarily a continuous one. In these circumstances, only the short-range diffusion of Ca and OH ions, through the overlapping layers of water vapour, can occur, but not the long-range diffusion which is possible only in completely water-filled blocks. Because of this short-range diffusion, the crystal growth will be localized. This localized anisotropic crystal growth, as observed in our experiments, will push apart the contacting particles, thereby creating and/or expanding the volume of pores in the block as had been found by Ramachandran et al. in their vapour-state hydration. As there will be a number of fine Ca(OH)₂ crystals available even after the complete hydration of CaO, the expansion will continue by the mechanism described in our original paper. Thus the main difference between the 'in liquid' and the vapour-state hydration is in the range of diffusion. In the first case the range is global and in the second it is local. In our experiments we have tried to simulate the localized diffusion by encasing the particles of CaO in a plastic matrix with a low permeability to water.

We do not believe that the hypothesis of a topochemical reaction in the vapour phase explains the facts, and the postulation of a gravity flow to explain the expansion of the sample after its complete hydration is an example of the difficulties involved in this hypothesis. In contrast, the simple effect of restricted range of diffusion, which will obviously occur in the vapour phase, is enough to explain why the formation of Ca(OH)₂ solution (albeit layer 'solution') and its crystallization give such different effects in the two cases, and covers all the facts without additional hypotheses of the 'gravity flow' type.

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