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The effect of moisture content upon the elasticity of hardened cement paste*

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It was with much interest that I read the paper by Dr Parrott. He seems to be suggesting that the increase in 'compliance' of partly dried Portland cement paste is due to the closing up of porosity created by C-spacing change of calcium silicate hydrate with drying. This suggestion is interesting and his results deserve further discussion.

In general, layer-structured calcium silicate hydrates alter their basal spacing with relative humidity, but their cross-sectional areas remain nearly unaltered. In other words, the percentage volume change is nearly the same as the percentage change in the basal spacing. For a paste composed of 100% calcium silicate hydrate, the volume shrinkage due to the basal spacing change from 14.5 to 13.0 Å will be 10.1% of the volume of calcium silicate hydrate. If the paste contains less than 100% calcium silicate hydrate, the volume shrinkage will be proportionately less. If this shrinkage is uniformly distributed, then the increase in 'compliance' due to the basal spacing change only is expected to be about 10%. However Figure 3 of the paper shows that the compliance has increased by about 100%. It will thus appear that some additional mechanism will be necessary to account for the observed increase in compliance.

In this context, some water permeability data of Powers et al. are of some interest⁽¹⁾. These authors carefully dried some Portland cement paste to 79%

R.H. in two stages and then re-saturated them to 100% R.H. The specimens did not show any microscopic crack. They found that the permeability coefficients of dried and re-saturated specimens were 70 times those of virgin companion specimens. In view of this large change of permeability coefficient, I will deal with this in some detail. In the following discussion, some 'order-of-magnitude' calculation will be done to illustrate some points. It is not to be assumed that Portland cement paste follows exactly the paths used in these calculations.

Any porous bed can be treated, on first approximation, as a bunch of parallel capillaries. The flow of water per second, Q , through such a bed will be given by⁽²⁾

$$Q = Kr^2A \frac{\Delta P}{L}$$

where K = a constant for a given fluid and temperature;

r = the average radii of the capillaries;

A = the total cross-sectional area of the bunch of capillaries;

ΔP = the drop in pressure across the bed;

L = the effective length of the capillaries.

What Powers et al. have actually found is that, for a given external size of specimen and a given ΔP , Q is 70 times more for the dried and re-saturated specimens than for companion specimens. In other words Kr^2A/L has increased by 70 times due to drying and

*Pages 17 to 20 of MCR 82.

re-saturation. Then, designating the re-saturated state as state 2 and the virgin state as 1, we can write

$$\frac{Q_2}{Q_1} = \frac{r_2^2 A_2 L_1}{r_1^2 A_1 L_2} = 70$$

To go any further, we have to assume that either (1) on being re-wetted to 100% R.H., calcium silicate hydrate has regained its original C spacing or (2) re-wetting does not re-hydrate calcium silicate hydrate to the original C spacing.

(1) On the first assumption, there is no change in volume porosity between state 1 and 2, i.e. $A_1 = A_2$. Then

$$\frac{r_2^2 L_1}{r_1^2 L_2} = 70$$

Now two extreme cases can be considered.

(a) On the assumption that no change has occurred in the radii of the capillaries due to drying, the effective length of the capillaries has been reduced by a factor of 70 in the dried specimens.

(b) On the assumption that the effective length of the capillaries has not changed,

$$\frac{r_2^2}{r_1^2} = 70$$

and

$$r_2 \approx 8r_1$$

In other words, out of the original eight capillaries,

seven have disappeared to make the last one eight times bigger. In both cases, the paste seems to have undergone drastic internal changes and the changes must have occurred *locally*, not uniformly.

(2) On the second assumption, that the calcium silicate hydrate crystals maintained their lower C spacing, volume porosity will increase by 10% of the volume of calcium silicate hydrate. This will increase the radii of the capillaries by a factor which will be a function of the original porosity. An order-of-magnitude calculation, for a paste with a original total porosity of 10%, will show that the effective length of the capillaries needs to be shortened by a factor of 15 to account for the increase in permeability coefficient. For higher porosity, this factor will be higher.

It appears that drying to 79% R.H. must have changed the flow channels drastically, by a factor of 10. It is a matter of semantics whether this order of rearrangement is called cracking, micro-cracking or increased porosity. However, this rearrangement is expected to make a large contribution to axial compliance.

Furthermore calcium silicate hydrate crystals in between the flow channels appeared to have been irreversibly brought closer during drying to make room for the alteration. This is consistent with the non-uniform consolidation proposed earlier⁽³⁾ on the basis of electron-microscopic evidence to explain irreversible shrinkage during first drying.

Reply by the author

I would like to thank Dr Chatterji for his discussion of my paper and comment upon the points that he has raised. Firstly, in case there is any misunderstanding, I should like to make it clear that the increase in 'compliance' was not thought to be associated with any 'closing up of porosity' as stated by Dr Chatterji but quite the contrary: I suggest that there may be an *increase* in porosity during first drying. I accept that some small proportion of hydrate particles might be brought into closer proximity as a result of drying but, as stated previously, consolidation would be expected to cause a decreased compliance rather than the measured increase. Thus consolidation is not thought to be a predominant mechanism in controlling elasticity.

Regarding the calculations to obtain effective changes in pore geometry that would be associated with the large permeability changes measured by Powers et al.⁽¹⁾ after first drying, I find it difficult to accept the idea of treating the pore system in hardened cement paste as parallel capillaries. I believe that the model suggested by Powers et al. wherein capillary pores become isolated cavities as hydration proceeds is more reasonable. It is then possible to account for the large changes of permeability with age that they

measured, and to explain the changes with drying. It was suggested by Powers et al. in reference 1 that drying may rupture some of the webs of gel between capillary cavities and thus greatly increase permeability. It seems quite possible that rupture of these webs, although increasing permeability, will not necessarily increase the compliance appreciably.

I do not fully understand the basis of Dr Chatterji's suggestion that shrinkage of the cement hydrates would only lead to a 10% increase in compliance, but it seems that this is a very conservative estimate. It is difficult to justify a quantitative model but, for an order-of-magnitude calculation, we can assume that compliance is proportional to $1/(1-p)^3$ where p is porosity. If, in addition, we assume an initial porosity of 0.5 and that drying reduces the volume of the hydrated solids without an appreciable bulk volume change, the calculated increase in compliance resulting from drying is about 40%. A large change in solid volume without a corresponding change in bulk volume would also cause disruption of bonds between hydrate particles and this, combined with the effect of any porosity change, could easily account for the observed change in compliance.

REFERENCES

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