Pergamon

Cement and Concrete Research, Vol 27, No 9, pp. 1451–1452, 1997

0008-8846/97 $17.00 + .00

PII S0008-8846(97)00131-2

A DISCUSSION OF THE PAPER "THE ROLE OF STERIC REPULSIVE FORCE IN THE DISPERSION OF CEMENT PARTICLES IN FRESH PASTE PREPARED WITH ORGANIC ADMIXTURE"* BY H. UCHIKAWA ET AL.

S. Chatterji
Carl Bernhardsvej 13B; St.4 1817 Frederiksberg C, Denmark

(Received May 15, 1997)

Prof. Uchikawa et al are to be congratulated for the beautiful demonstration of the steric repulsive force utilizing atomic force microscope (AFM). Further more they have also supplied us with some quantitative data on some organic admixtures in relation to the steric repulsive forces they may produce in freshly made cement pastes. Like all good papers this paper allows other researchers to draw some inferences and raise some questions which could not have been done previously. I would like to draw a few inferences and raise a few such questions and would be much interested to know Prof. Uchikawa et al's opinion of them.

For easy reference I have collected the relevant parts of the paper in the following:

i) A Portland cement of 3,350 cm^2/g Blaine surface was used.
ii) Of the three organic admixtures used two, PC-A and PC-B, have been further characterized. PC-A, a branched chained polycarbonate, has its main and side chains approximately 30 and 20 nm long. PC-B is a linear polycarbonate approximately 154 nm long. The third admixture NS, of a mean molecular weight of 1,400, has not been characterized any further; although from its structure it should be linear.
iii) 10% solutions of the organic admixtures were used in the experiments with AFM.
iv) An active component of admixture/cement weight ratio of 0.6% was used for the measurement of Zeta Potentials in cement pastes of w/c ratio 0.3. Presumably, although it is not stated, the same admixture/cement and w/c ratio were also used in the measurement of the flow properties of the cement pastes.
v) From Fig. 5 it can be seen that the interaction between the AFM probe and polished clinker test specimens, immersed in 10% solutions, starts at a separation of about 500 nm for PC-A, at 150 nm for NS and at 125 nm for PC-B. Once started the Interactive force increases with decreasing separation between the AFM probe and test specimen.

AFM Studies

On a simplifying assumption that, in an admixture solution of a given strength, the adsorbed layers both on the silicon nitride AFM probe and on polished clinker have similar characteristics the effective thickness of the adsorbed layers may be estimated for each admixture from (v) as one half the separation at the beginning of interaction. For 10% solutions these

*Cem. Concr. Res. 27, 37–50 (1997)

thicknesses are 75, 63 and 250 nm for NS, PC-B and PC-A respectively. Comparing these layer thicknesses with the length characteristics of the admixtures one may infer that in the adsorbed layer NS is mainly anchored to the clinker surface by one end of the molecules and its mean effective length is about 75 nm; for PC-B the adsorption is of train, loop and tail type with the average tail-loop height is about 60 nm. For both NS and PC-B the adsorbed layers are mainly mono-layers. For PC-A the adsorbed layer is either 8 or 12 layer thick depending on the orientation of the molecule in the layer i.e. multi-layer adsorption occurred. PC-A is a copolymer of acrylic acid with acrylic ester. Could it be that this copolymer has separated out as emulsion particles from concentrated $Ca(OH)_2$ solution at the clinker surface forming 250 nm thick layers of the emulsion particles? In that case the Interactive force is partly a measure of the compressibility of the emulsion particles.

Flow Properties

On the assumption that Prof. Uchikawa et al have used a 0.6% active polymer/cement ratio by weight in their pastes for the measurement of flow properties (this is within the range of practical dosage) the following calculations could be carried out. 100 g cement has a surface of 33.5 m^2. Densities of the active components of the admixtures are not known; however, most purely organic compounds have densities of about 1. On this basis the volume of 0.6 g admixture is 600×10^{-9} m^3. An uniform surface coverage of unhydrated cement gives a layer of 18 nm thickness for the admixtures. Even a realistic surface coverage of 50% i.e taking care of unavailable surface in between the admixture molecules, gives a layer thickness of 36 nm. This indicates that PC-A forms a mono-layer thick absorption layer and NS and PC-B either form non-uniform layers or their adsorption changed to train type adsorption. The increased flow characteristics indicates to the train type adsorption. The inferences about the variation in the orientations of admixture molecules in the adsorbed layers with their concentrations could not have been drawn without the quantitative data of Prof. Uchikawa et al; although on hindsight they appear reasonable. In any case the beginning of interaction distances are expected to change from those in 10% solutions. How will the Interactive force-Distance characteristics change?

In the practical use of admixtures the enhanced flow is maintained over about 45 minutes or so. However, it is known that admixture molecules, at least NS type, get fully adsorbed within about 5 minutes of paste making. With continued formation of hydration products, most of which have no organic polymer coating, how is the flow maintained over such long period?