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**A REPLY TO THE DISCUSSION BY SUSANTA CHATTERJI OF THE PAPER  
"THE ROLE OF STERIC REPULSIVE FORCE IN THE DISPERSION OF  
CEMENT PARTICLES IN FRESH PASTE PREPARED WITH  
ORGANIC ADMIXTURE"\***

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Thank you so much for showing deep interest in our paper and for giving us useful suggestions. Our opinions on the questions submitted to use will be mentioned hereafter.

### **1. AFM Studies**

#### 1) Evaluation of thickness of adsorption layer

In this paper, the repulsive force was measured on the surface of alite predominating in the surface of cement clinker.

The results of this study indicate that the force acting on the cement particles generated by adding the mixture, "PC-A," is mainly a steric repulsive force. Since the steric repulsive force is generated by the overlapping of the adsorption layers of admixture adsorbed to the surface of cement particles, "Thickness of adsorption layer is nearly equal to the half of the action distance of repulsive force" is applied without great error.

Meanwhile, the electrostatic repulsive force predominates in the force of action in the case of adding NS and PC-B. Since the electrostatic repulsive force is generated by the electric double layer extending outside the adsorption layer of admixture as shown in Fig. 2 in that paper (1), the electrostatic repulsive force is generated even though the adsorption layers of admixture do not overlap with each other. It is, therefore, considered that the thickness of the adsorption layer of admixture is smaller than the half of the action distance of repulsive force.

The thickness of the adsorption layer of admixture can be measured either by AES or AFM. We have already reported on the thicknesses of the adsorption layers of NS and LS (lignin sulfonic acid-based admixture) on the surface of cement clinker minerals (2)(3)(4). The result indicated that the thickness of the adsorption layers of those admixtures on the surface of cement clinker were not so much changed though the contents of them were changed in a range of 2% or less each. The thicknesses of the adsorption layers of NS and LS on the surface of alite were approximately 50 and 100nm, respectively.

The thickness of the adsorption layer of admixture on the interstitial materials including  $C_3A$  solid solution is larger than that on alite, depending upon the types of admixtures. Although the thickness of the adsorption layer estimated from the measurement of the repulsive force in this paper cannot be directly compared with that determined by AES

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\*Cem. Concr. Res. 27, 37-50 (1997)

because of the difference of experimental conditions, it is considered that the latter is useful for reference.

## 2) Estimation of adsorption state

Considering from the thickness of the adsorption layer and the length of molecule of PC-A, it is reasonable to estimate that the adsorption state is regarded as multi-layer adsorption agreeing with Dr. Chatterji's view.

It is considered that the thickness of the adsorption layer is smaller than the half of the action distance of repulsive force in the case of adding PC-B. Considered from this as well as the length of molecule of PC-B, therefore, the adsorption state may belong to the train-loop-tail type as Dr. Chatterji stated.

The length of molecule of NS calculated from the mean molecular weight is approximately 2.7nm and the thickness of the adsorption layer is smaller than the half of the acting distance of repulsive force as mentioned above. The thickness of the adsorption layer is, therefore, to be 20 times as large as the length of molecule. So the adsorption state is probably to be the multi-layer adsorption.

Although the adsorption state of NS has been considered so far that it is adsorbed to a cement particle as stacking form at the part of naphthalene ring, it is difficult to estimate how the admixture is adsorbed to the cement particle because the benzene rings composing naphthalene ring may be distorted at the bonding site. It is, therefore, important to obtain reliable experimental evidence on the adsorption state by any method.

## 3) Possibility of emulsion formation of PC-A

Although the definition of emulsion stated by Dr. Chatterji cannot be exactly understood, there is no denying the possibility that PC-A formed composed of microgel. Since macro-molecular compounds including admixtures generally assume various conformations in water, the performance of them is largely affected. We will try to determine the conformation of the admixture by observing the expansion of the macro-molecular compounds in water by suitable method such as light-scattering near future.

# **2. Flow Properties**

## 1) Effects of the concentration of admixture on F-D characteristics

It has been confirmed by a preliminary experiment that the F-D characteristics are not so much affected by the concentration of admixture ranging from 1 to 20%.

## 2) Change of flow with time

The fluidity of concrete is generally lowered with the passage of time even an admixture is added to cement. However, the change of the fluidity of concrete with time has recently been remarkably reduced by the improvement of the admixtures, mainly because of the mixing of slow- and late-releasing agents. The slow- and late-releasing agents are produced by dewatering and esterifying the main components of admixtures and polymerizing the reaction products. The slow- and late-releasing agents are water-soluble though they don't have dispersibility just after the contacting with water. The esteratic site in those agents are hydrolyzed into the same substances as the main components of the admixtures by the reaction of  $\text{Ca}^{2+}$  and alkali ions dissolved from cement with the processing of the hydration

reaction of cement. The hydrolysis-derived substances are adsorbed to the delayed-produced hydrate particles and disperse them, thereby keeping the fluidity of cement paste. Many recently developed admixtures contain the components for sustaining the slump such as slow- and late-releasing agents as well as the components for improving the dispersibility just after the mixing.

### References

1. H. Uchikawa, S. Hanehara and D. Sawaki, *Cem. Concr. Res.* 27, 37-50, 1997.
2. H. Uchikawa, S. Hanehara, T. Shirasaka and D. Sawaki, *Cem. Concr. Res.* 22, 1115-1129, 1992.
3. H. Uchikawa, D. Sawaki and S. Hanehara, *Cem. Concr. Res.* 25, 353-364, 1995.
4. H. Uchikawa, Conference in tribute to Micheline Moranville Regourd held in Sherbrooke, Canada on October 6, 1994.