adsorbed to binding materials with different specific surface areas was considered. The molecular size and number of polycarboxylate-based dispersant molecules adsorbed were estimated, based on the measurements of the specific surface area of polycarboxylate-based dispersant, its chemical structure and average molecular weight of the dispersant polymer.

EXPERIMENTAL DETAILS

MATERIALS

(1) Binding materials

3 types of cement, 4 types blastfurnace slag and 6 types of lime stone particles were used in the tests. Table 1 shows the chemical composition of the materials. We studied limestone fine particles, although this is not generally included in the class of binding materials.

a) Cement

Commercialized normal portland cement (NPC), early strength cement (ESC), moderate heat generation cement (MHC), low heat generation cement (LHC) classified into 6 to 26 μm fineness by the Society for the Study of Cement-Based Material Design Support Systems were used.

b) Blast furnace slag fine particles

The specific surface area of the four types of blast furnace slag fine particles (BF) ranged from 4,000, 6,000, 8,000 and 10,000 cm^2/g .

c) Limestone fine particles

Six types of commercial limestone fine particles (NF) and 5 types of limestone fine particles (LS) with specific surface areas of 3,500, 4,700, 8,900, 11,000, and 20,000 cm^2/g were used.

(2) Dispersant

Polycarboxylate-based dispersant (acrylic acid-based: PA), a dispersing component in polycarboxylate-based superplasticizers, was used. The average molecular weight measured by GPC analysis was 26,000 in terms of PEG equivalent. Fig. 1 shows the chemical structure of PA.

TEST METHODS

(1) Measurement of specific surface area

We measured the specific surface areas of the binding materials by measuring both the BET specific surface areas using the nitrogen gas adsorption method, and the specific surface area by the Blaine method.

(2) Measurement of adsorption amount

Cement paste with W/C = 35% (cement content 500 g, mixing water containing dispersant 175 g) was mixed for 3 minutes with an ASTM mortar mixer. A suction filter filtered off the liquid phase. The organic carbon content in the filtrate was determined with a total organic carbon analyzer (Shimadzu TOC 5000). The adsorbed amount of dispersant to the binding material (apparent adsorbed amount) was calculated by subtracting the dispersant amount calculated from the carbon content in the filtrate, from the dosage of dispersant.

The number of adsorbed dispersant molecules was estimated by calculating the adsorbed amount per unit area based on the BET specific surface area value, and subtracting the Avogadro number (N_A) from the molecular weight of the dispersant polymer.

RESULTS AND DISCUSSIONS

Size of the polycarboxylate-based dispersant

The size of the PA polymer was calculated based on the chemical structure and molecular weight of the PA polymer. Fig. 2 shows the length of polymer conformation that is adopted as a basis for the calculation. The length of C-C-C in the main chain was assumed to be 2.51Å, thid is the maximum streched length of 3 carbon atoms according to the literature (5). The length of an ethylene glycol side chain, according to the literature (5), is 19.5Å for a 7-unit chain elongated in a stable condition. The length of the trunk polymer when stretched to its maximum length was calculated to be 20 nm, with a side chain length of 7 nm (Fig. 3 (a)) by Figure. 1 (a=25,n+m=70).

If PA is sufficiently stretched in water, the trunk polymer can freely rotate and the side chains extend in 3 dimensions. This rotation means that the effective length covered by the side chains is 14 nm, twice the original length (Fig. 3 (b)). However, when PA is adsorbed on to the particle surface of the binding material, most side chains reach out towards the water. The size of the dispersant at that time is presumed to be as shown in Fig. 3(c). The volume occupied by the molecule when it freely moves is equivalent to a column 7 nm in thickness and 20 nm in length. The thermodynamic effective volume of the column is as large as the volume of a cylinder with diameter of 20 nm and a height of 7 nm (Fig. 3(d) (6). Due to the size of the molecule stretched to its full length, based on the molecular weight of the polycarboxylate-based dispersant, it is considered that one dispersant polymer occupies the volume of a cylinder with 20 nm in diameter and 7 nm high, excluding other molecules. Therefore, at a state of saturated adsorption the density of adsorption is believed to be one molecule of dispersing polymer molecule per 400 nm^2 of the binding material surface (Fig, 3(d)).

Specific surface area of binding materials

The results of measurements of the specific surface areas of binding materials by the BET and Blaine methods are given in Table 2. A comparison of the specific surface areas by the BET and Blaine methods is given in Fig. 4. There is a good correlation between the specific surface areas by the BET and Blaine method, even in the high range of the specific surface area.

Adsorbed amount of dispersant to binding materials

The dosage of the dispersant is fixed to 0.15% of the mass of the binding material. Table 2 shows the adsorbed amount to binding materials in terms of per unit weight and per unit surface area. In previous papers, the adsorbed amount had been calculated based on the specific surface area by the Blaine method (3),(4), however, in this paper it was calculated based on the specific surface area by the BET method that can measure the micro structures of the surface of binding materials.

Adsorbed number of dispersant to binding materials

Based on the adsorbed amount per unit surface area, and the molecular weight of the dispersant, a number A of adsorbed molecules of dispersant per unit area of binding material was calculated.

$$A = B / Mw \times N_A \quad [1]$$

Where A: adsorbed number of PA per unit area
B: adsorbed amount of PA per unit area
N_A: Avogadro number = 6.02×10^{23}
Mw: Weight-average molecular weight

Results are given in Table 2. The numbers of molecules of dispersant adsorbed per unit area varied with the type of binding material. The number of PA molecules adsorbed on every 100 nm^2 surface area of cement is the highest with 2.2 to 3.2, the next is BF with 1.2 to 1.9, and the lowest is LS with 0.8 to 1.2.

NPC and ESC which exhibit higher reactivity after contact with water, adsorb a comparatively higher number of PA molecules per unit area than do MHC and LHC. This suggests that the number of adsorbed PA per unit surface area is relating to reactivity just after water contact. It is reported that the surface area of OPC increase by 2 to 2.5 times just after water contact (7). Considering this fact, 1 to 1.5 molecules of PA are believed to be adsorbed per 100 nm^2.

Consideration on the state of adsorption of PA onto the surface of binding materials

Binding particles produce fractal surface structures. It was presumed that the adsorption form of PA cannot follow the fraction of the surface structure, so the adsorbed number of PA per unit surface area decreases compared with the number that is calculated at 3.1 at the maximum molecular extension (1 molecule per 400 nm^2 = 0.25 molecule per 100 nm^2).

The experimental value indicated that 0.8 to 3.2 molecules of PA were absorbed per 100 nm^2, a figure higher than expected. The cause of the higher adsorbed of PA molecules to the surface of binding material is considered to be due to multi-layer adsorbtion or shrinkage of PA molecules. However, the relationship between the dosage and adsorbed amounts of (2), (3), and (4) that had been conducted, as seen in Fig. 5, does not indicate a multi-layer adsorbed because the adsorbed amount increases after adsorption is saturated, therefore multi-layer adsorption is not considered to have occurred.

It was previously reported, as shown in Fig. 6, that the measurement results of the root mean square radius of the molecular by a light scattering method indicates that the PA polymer shrinks to 70 to 50% as the sulfate ion concentration increases (4). It follows that the PA polymer with a main chain that has shrunk to 70 to 50% of the maximum extended length adsorbs to the surface of the binding materials (Fig. 7(a)). This also suggests that polymer molecules overlap even in the range of stable entropy (Fig. 7 (b)). Since it is also presumed that PA is adsorbed even to BF and LS that elute only small amount of sulfate ion, factors other than sulfate ions need to be studied.

CONCLUSIONS

1) Calculations of the polymer size based on the chemical structure and molecular weight of PA polymer indicate that the full length of PA polymer in the direction of trunk polymer is 20 nm and that in the side chain direction is 7 nm.

2) Considering the thermodynamic effective volume, one PA polymer adsorbs in every cylindrical volume with a diameter of 20 nm and a height of 7 nm.

3) Calculations based on the measurement results of actual adsorption volume indicate that 1 to 3 PA polymer molecules adsorb to every 100 nm^2 surface of binding materials.

4) Sulfate ions cause PA polymer molecules to contract, and become densely adsorbed on the surface of the binding materials.

ACKNOWLEDGEMENTS

In the measurement of BET specific surface area by nitrogen adsorption of various types of binding materials and non-reactive admix materials, we acknowledge the assistance of Messrs. Takaharu Goto and Naoshi Ozawa, researchers of Sakura Central Research Laboratory of Taiheiyo Cement Corporation.

REFERENCES

1. Yoshioka, K. et al., “ Role of Steric Hindrance Effects of Superplasticizer on the Dispersibility of Cement Particles, ” Proceedings of the Japan Concrete Institute, Vol. 19, No. 1, pp.335-340 (1997)
2. Ohta, A. Sugiyama, T. and Tanaka, Y., “Fluidizing Mechanism and Application of Polycarboxylate-based Superplasticizers,” Fifth CANMET/ACI, Superplasticizers and Other Chemical Admixtures in Concrete, pp. 358-378 (1997)
3. Ohta, A. and Uomoto, T., :“Study on the Dispersion Mechanism of Polycarboxylate-based Dispersing Agent” Cement Science and Concrete Technology, No. 52, pp. 138-143 (1998)
4. Ohta, A. and Uomoto, T., “Study on the Dispersing Effect of

Polycarboxylate-based Dispersing Agent to Binding Materials," Proceedings of the Japan Concrete Institute, Vol. 19, No. 2, pp. 85-90 (1998)

5. Tadokoro, H., "Structure of Polymer," p.18, p.106 (1976)
6. *Colloid Science I, Basic and Dispersion and Adsorption*, Japan Chemical Society pp. 263-264
7. Uchikawa, H. et al., "Influence of $CaSO_4 \cdot 2H_2O$、$CaSO_4 \cdot 1/2H_2O$, $CaSO_4$ on the Initial Hydration of Clinker Having Different Burning Degree," *Onoda Research Report*, Vol. 36, Book 2, No. 112, pp.55/67, (1984)

Akira Ohta is Dr. Eng., Group Leader of Admixture Group 1, Central Research Laboratories, NMB Co. Ltd. His research interests include chemical synthesis of various polymer dispersing agents, evaluation of their performance, and material science.

Tomomi Sugiyama is a research chemist at Central Research Laboratories, NMB Co. Ltd. His research interests include the chemical analysis of admixtures and material science.

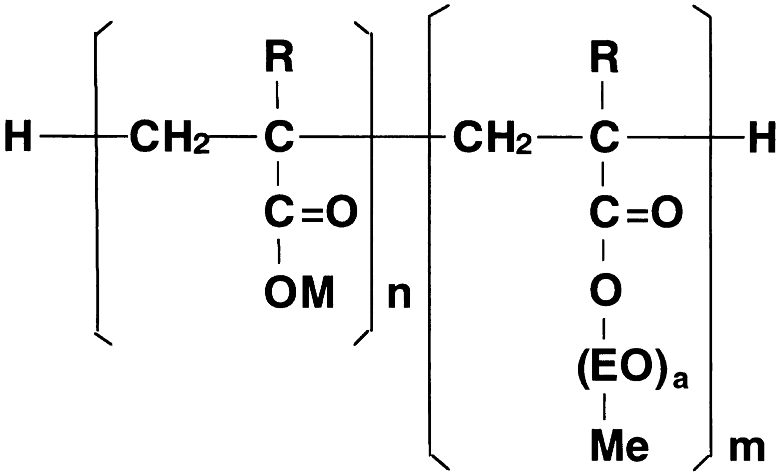
Taketo Uomoto is a member of the Center for Collaborative Research, University of Tokyo, Japan. He specializes in durability of concrete, nondestructive testing, new composite materials, analytical computer modeling phenomena, and durability of shotcrete.

Table 1 Chemical conposition of binders

Binder		ig. loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO3	$CaCO_3$
		mass %							
Cement	OPC	-	21.2	5.1	3.0	64.9	1.6	1.9	-
	NPC	0.34	22.1	5.0	3.0	66.3	1.5	0.5	-
	ESC	0.40	21.5	4.8	2.8	67.3	1.8	0.4	-
	MHC	0.43	23.2	3.8	5.0	65.6	1.0	0.3	-
	LHC	0.34	26.4	3.4	3.3	64.9	1.2	0.4	-
Blast furnace slag	BF-4000	-	32.1	13.2	0.2	42.5	6.6	2.1	-
	BF-6000	-	33.1	12.6	0.2	42.7	6.5	2.1	-
	BF-8000	-	32.1	14.2	0.1	42.9	6.1	2.0	-
	BF-10000	-	32.6	12.9	0.2	42.6	6.6	2.0	-
Lime stone powder	NF	-	0.3	0.1	0.0	55.3	0.3	0.0	97.3
	LS-3500	-	1.9	0.2	0.2	53.7	0.8	0.0	95.8
	LS-4700	-	0.5	0.1	0.1	54.9	0.5	0.0	98.0
	LS-8900	-	2.7	0.2	0.2	53.3	0.9	0.0	95.3
	LS-11000	-	2.7	0.2	0.2	53.3	0.9	0.0	95.1
	LS-20000	-	1.7	0.1	0.2	54.0	0.8	0.0	96.3

Table 2 Surface area of binders and adsorbed amount of PA

Binder		Surface Area		Adsorbed Amount		Adsorbed Number per Unit Area (N/100nm^2)
		Blaine method (cm^2/g)	BET Method (m^2/g)	per Unit Weight (mg/g)	per Unit Area (mg/m^2)	
Cement	OPC	3250	0.715	0.84	1.17	2.71
	NPC	2920	0.695	0.96	1.39	3.20
	ESC	3460	0.772	0.95	1.23	2.84
	MHC	2770	0.817	0.77	0.94	2.17
	LHC	3150	0.715	0.49	0.68	1.58
Blast furnace slag	BF-4000	4110	0.868	0.70	0.81	1.86
	BF-6000	5810	1.212	0.84	0.69	1.60
	BF-8000	7960	1.729	1.09	0.63	1.46
	BF-10000	9800	2.368	1.25	0.53	1.22
Lime stone powder	NF	5440	1.357	0.58	0.43	0.99
	LS-3500	3480	0.876	0.32	0.37	0.84
	LS-4700	4730	1.029	0.38	0.37	0.85
	LS-8900	8380	1.868	0.95	0.51	1.17
	LS-11000	10970	2.451	0.91	0.37	0.86
	LS-20000	18180	4.061	1.92	0.47	1.09



$$H-\left[CH_2-\overset{R}{\underset{\underset{OM}{|}}{\underset{C=O}{\underset{|}{C}}}}\right]_n-\left[CH_2-C(R)(C(=O)-O-(EO)_a-Me)\right]_m-H$$

R=H,Me
M: Metal, EO: Ethylene oxide,
Me: Methyl

Fig. 1 Chemical structure of PA

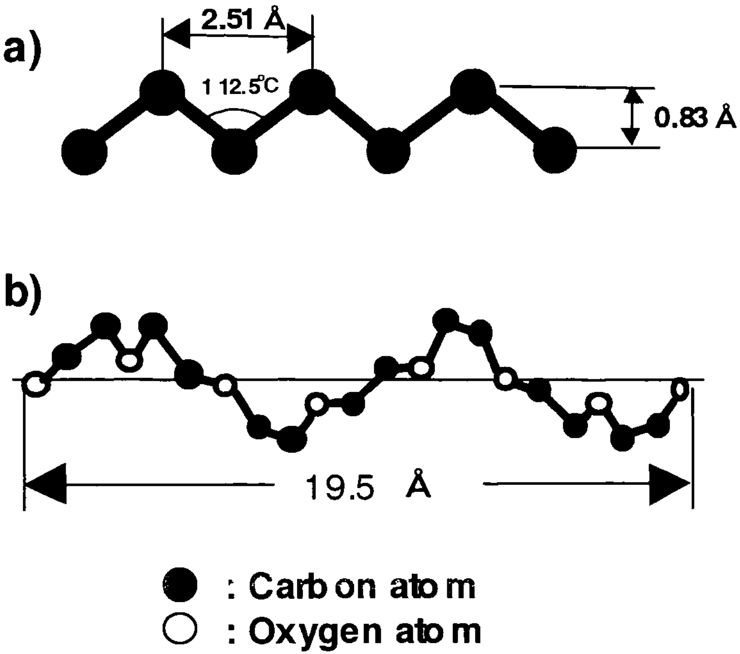


Fig. 2 Stable conformation of a) Polyethylene and b) Polyethylene oxide