

# Influence of sulfonated naphthalene on the fluidity of cement pastes

## *Influence de la naphthaline sulfonée sur la fluidité des pâtes de ciment*

M. COLLEPARDI, Professor of Materials Technology and Applied Chemistry,  
 M. CORRADI, Doctor in Industrial Chemistry,  
 G. BALDINI, Doctor in Industrial Chemistry and  
 M. PAURI, Doctor in Industrial Chemistry,  
 Department of Materials Science, University of Ancona, Italy  
 Research and Development Laboratory, MAC Mediterranea Additivi Cementi, Treviso, Italy.

**RÉSUMÉ :** On a examiné, grâce à un test de mini-slump, l'influence de la naphthaline sulfonée (monomère) et de la naphthaline-sulfonée-condensée (polymère) sur les propriétés rhéologiques des pâtes de ciment. L'influence du moment de l'addition de ces produits sur la fluidité des pâtes de ciment a également été étudiée.

Les mesures d'adsorption, de potentiel Zéta, de calorimétrie, de diffraction de rayons X et d'analyse thermique ont été effectuées sur les pâtes de ciment/

En ajoutant une dose inférieure à 0.5 % en poids du ciment de polymère en poudre, on augmente notablement la fluidité de la pâte, alors que l'hydratation du ciment reste pratiquement la même. Des dosages supérieurs en polymère (1 - 1,5 %) augmentent la fluidité de façon négligeable et provoquent un retard de l'hydratation du ciment durant la période d'induction. Par contre, l'addition du monomère ne provoque aucune modification significative de la fluidité ou de l'hydratation.

Le moment de l'addition du polymère influence également la fluidité des pâtes de ciment et la vitesse d'hydratation durant la période d'induction. On a observé d'intéressantes relations entre l'adsorption du polymère, le potentiel Zéta et la fluidité de la pâte de ciment.

### SUMMARY :

The influence of sulfonated naphthalene (monomer) and sulfonated naphthalene condensate (polymer) on the rheological properties of cement pastes determined by mini-slump test was examined. The influence of time of addition of these products on the fluidity of the pastes was also studied.

Adsorption, zeta potential, calorimetry, XRD and thermal analysis (DTG) were also carried out on the cement pastes.

With dry polymer additions lower than 0.5 % by weight of cement, fluidity of the paste is remarkably increased, whereas the cement early hydration is substantially the same. Higher dosages of dry polymer (1 - 1.5 %) increase fluidity to a lower extent and cause stronger retardation in the cement hydration during the induction period. Conversely, no substantial change neither in the fluidity nor in the early hydration rate was caused by the addition of the monomer.

The time of addition of the polymer also affects the fluidity of cement pastes, and the cement hydration rate during the induction period, increasing fluidity and retarding the cement hydration. Some interesting relationships between polymer adsorption, zeta potential, and paste fluidity were found.

## INTRODUCTION

All the properties of the hardened concrete proportionally improve by reducing the water/cement (w/c) ratio of the fresh mix. However, the w/c ratio cannot be decreased under certain limits because of the reduction in the workability of the fresh concrete. The so-called super-water-reducers or superplasticizers can be used as additives that permit a concrete to have about 25 % of the mixing water removed without reduction in workability or a strong increase in workability (for example : from 20 mm to 220 mm in slump) without a significant change in all the properties of the hardened concrete. Combination of the two effects can also be obtained.

A large number of works has been devoted to study the properties of fresh and hardened concrete containing commercial superplasticizers (1). However, relatively few papers have been published to explain the effect of the superplasticizers on the water-cement system. In particular, few data (2-6) have appeared about the effect of pure chemical products used as superplasticizers on the physical-chemical changes of the cement pastes.

Superplasticizers are substantially based on sulfonated naphthalene-formaldehyde polymers or sulfonated melamine-formaldehyde polymers (7). The purpose of the present paper is to examine the influence of sulfonated naphthalene as a monomer and sulfonated naphthalene formaldehyde condensed polymer on the physical-chemical properties of a cement paste. Moreover the effect of the time of addition of the additives on the same properties were also studied.

## EXPERIMENTAL

Materials

Ordinary portland cement was used and Table 1. shows its chemical analysis. Pure sodium salt of naphthalene sulfonic acid (monomer) and sodium sulfonated naphthalene formaldehyde condensate (polymer) both produced as dry powders by MAC Spa were utilized. An aqueous solution of the sulfate-free polymer (wt % solid = 40) shows a viscosity of 40 cp and a specific gravity of 1.224 g/cm<sup>3</sup> at 20°C. Tap water with a specific conductance of 480 mho . cm<sup>-1</sup> was used.

Table 1 - Chemical analysis of cement

SiO <sub>2</sub>	=	20.80 %
Al <sub>2</sub> O <sub>3</sub>	=	5.51 %
Fe <sub>2</sub> O <sub>3</sub>	=	2.99 %
CaO	=	63.60 %
MgO	=	0.85 %
K <sub>2</sub> O	=	0.38 %
Na <sub>2</sub> O	=	0.19 %
SO <sub>3</sub>	=	1.75 %

L <sub>2</sub> O. I. (950°C, 1h)	=	2.00 %
Blaine surface area	=	3.850 cm <sup>2</sup> /g

Cement pastes were prepared at 20°C by mixing for 5 min 50 g of cement and enough water to obtain w/c ratio of 0.3 or 2. In a first series of experiments the monomer or the polymer were added to cement with mixing water. In a second series of experiments the solid additives were added 2.5 min after mixing and then the pastes were mixed again for other 2.5 min. Both polymer and monomer additions are expressed as percent by weight of cement. It must be taken into account that commercial superplasticizers are aqueous solutions generally containing from 20 to 40 % of the dry polymer used in the present work.

Techniques

The following experiments were performed : Minislump tests, polymer adsorption on cement, zeta-potential, isothermal calorimetry, X-ray diffraction analysis (XRD), differential thermal gravimetry (DTG). All the measurements were carried out at 20°C with polymer or monomer addition with mixing water or after 2.5 min the mixing had begun.

In the minislump tests (8) the pastes were prepared only with w/c ratio of 0.3, adding each time a different dosage rate of polymer or monomer, and the pat areas (in cm<sup>2</sup>) were measured after five minutes of mixing.

The magnitude of surface adsorption of the monomer or the polymer upon the cement particles was determined by U.V. absorption spectroscopy in the 220-230 nm absorption band due to a sulfonated naphthalene group present in both the polymer and the monomer. Fifty grams of cement and 15 ml (w/c = 0.3) or 100 ml (w/c = 2) of polymer or monomer solution of known concentration were mixed continuously for 5 minutes. In the delayed addition tests the dry polymer or the monomer was added after 2.5 min of mixing with tap water and then the paste was mixed again for other 2.5 min.

The liquid phase was then separated by filtration under vacuum. Each solution was diluted to the optimum concentration and brought to pH 6.5 before spectroscopic measurement. The quantities adsorbed were calculated by differences in concentration of polymer or monomer of the liquid phase before and after adsorption.

The zeta potential measurements were performed using a Laser Zee Meter by Pen Kem Inc. which is based on electrophoretic technique (9) and gives the results directly in millivolt. Zeta potential of colloidal particles is measured by determining the rate at which these particles move in a known electric field.

Zeta potential measurements were performed only with w/c ratio of 2. The samples for the measurements were prepared by mixing continuously 50 g of cement, 100 ml of water and a certain amount of additive for 5 minutes, then separating the liquid phase by vacuum filtration. Small portion of original paste was added to the filtered liquid phase and a suspension (0.5 g of solid/liter) was obtained with the same ionic

strength of the original paste and diluted enough to be observed to the microscope of the Laser Zee Meter.

Heat evolution as a function of time was determined according a method previously described (10) by using an isothermal conduction calorimeter. In the delayed addition tests, the polymer or the monomer was added after 2.5 min by injecting a saturated water solution so that the resulting final w/c ratio was 0.3, and then mechanically vibrating for 2.5 min.

XRD and DTG analysis were also performed on the hydrated cement pastes with a w/c ratio of 0.3.

#### DISCUSSION OF RESULTS

In fig. 1 the influence of monomer and polymer additions on the flowability of cement pastes measured by the minislump test is shown. No substantial change in the flowability is recorded by adding the monomer both in mixing water and after 2.5 min of mixing, whereas very drastic increase in the minislump is caused by the polymer. However, the influence of the polymer is quite affected by the time of addition.

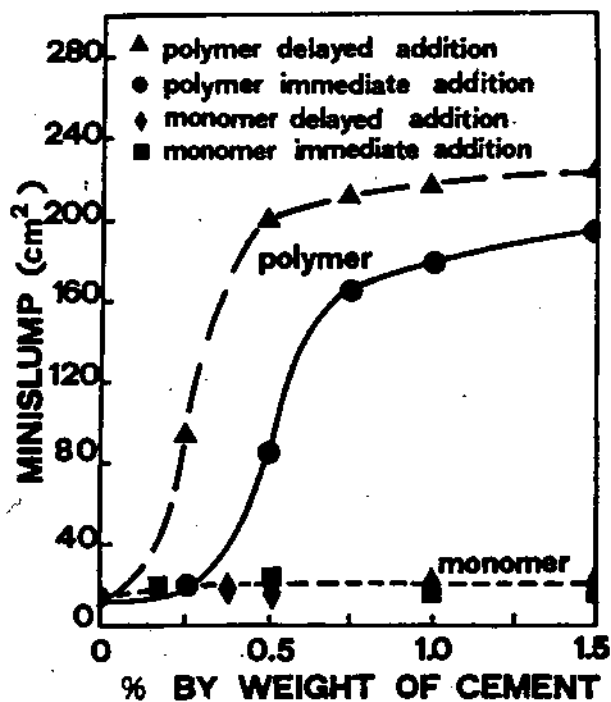


Fig. 1 - Influence of polymer or monomer addition on flowability (minislump) of cement pastes (w/c = 0.3).

A delayed addition of the polymer seems to be more effective particularly in the lower dosage range. For example, 0.25 % of polymer raises the minislump from 15 cm<sup>2</sup> to 95 cm<sup>2</sup>, when the admixture is added to the cement paste after 2.5 min after mixing had begun, while a negligible increase (from 15 cm<sup>2</sup> to 20 cm<sup>2</sup>)

is observed if the same amount of polymer is added with the mixing water. With a delayed addition of 0.5 % of polymer, the minislump rises to 200 cm<sup>2</sup>, while no significant further increase is recorded with higher amounts of additive. On the other hand, the minislump arrives at 160 cm<sup>2</sup> if about 0.75% of polymer is added with the mixing water, with only minor changes in flowability for higher percentages of addition.

In Fig. 2 the amount of polymer or monomer adsorption by cement as a function of the percentage of admixture added to cement paste is shown. The polymer is much more adsorbed than the monomer. Moreover, the adsorption of the polymer depends on the w/c ratio of the paste and on the time of addition, whereas these parameters do not substantially affect the adsorption of the monomer.

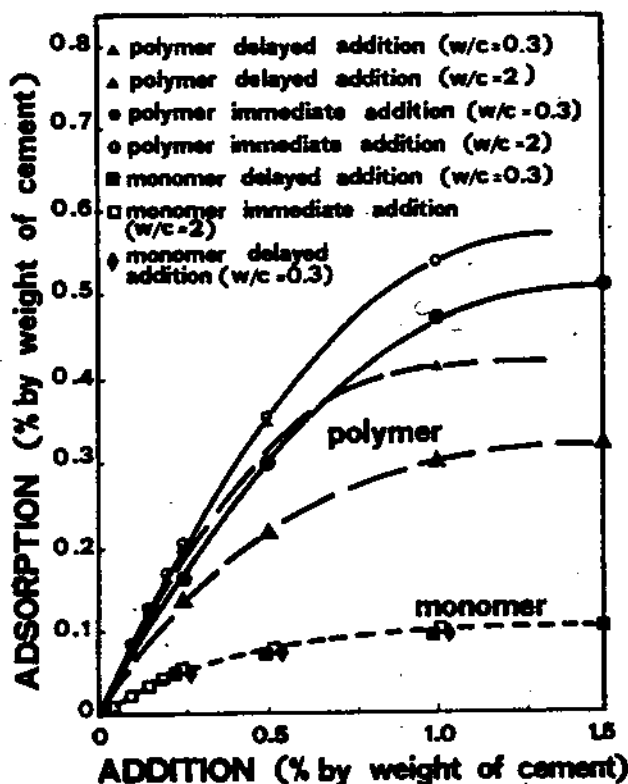


Fig. 2 - Polymer or monomer adsorption on cement as a function of addition.

Polymer adsorption appears to be higher with a higher w/c ratio whereas one would expect the contrary due to the greater polymer concentration in the aqueous phase of the paste with a lower w/c ratio (0.3). Three mechanisms, all related to the larger amount of mixing water, could possibly explain the higher adsorption in the paste with a higher w/c ratio: a) a larger amount of hydrated cement; b) a better dispersion of cement

particles; c) a lower concentration of ions coming from cement phases that could interfere with the polymer adsorption.

Adsorption seems to be greater when the polymer is immediately added with the mixing water. It is possible to think that the polymer adsorbed by cement particles in the early stage of hydration is coated by initial hydration products such as ettringite, and in this way it becomes unaffactive in terms of electrical surfaces properties. By this way the nominal adsorption, calculated by difference between the polymer concentration in water before and after mixing with cement, really includes a certain part of polymer incorporated in the hydrated products of cement. Moreover, when the polymer addition is delayed, there is a much higher concentration of ions coming from cement and these could interfere with the polymer adsorption to a greater extent.

Fig. 3 shows the ratio between the concentration of admixture in the liquid phase after and before the

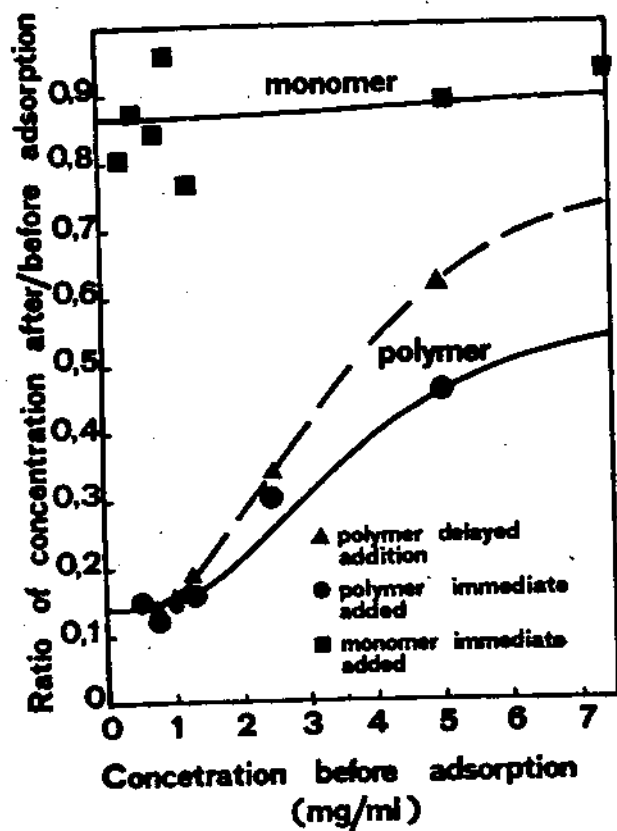


Fig. 3 - Relationship between the admixture concentration in the liquid before and after adsorption ( $w/c = 2$ ).

adsorption experiments (after/before) as a function of the initial concentration (before) for both polymer and monomer. The after/before concentration ratio is substantially constant for the monomer indicating that

about 85 % of the product always remains in the liquid phase. On the other hand, the after/before concentration for the polymer decreases by decreasing the polymer initial concentration in the liquid phase. However this ratio tends to about 0.15 by extrapolating the initial concentration to zero. Daimon and Roy (5) found 0.20 for the extrapolated value of the after/before concentration ratio and concluded that 20 % of their original admixture (sulfonated naphthalene formaldehyde condensate) was to be considered unadsorbable. By assuming that the monomer is the only unadsorbable impurity present in the "polymer", one could conclude that the percentage of monomer is about 23.5 % ( $= 20/0.85$ ) in the sulfonated naphthalene formaldehyde condensate used by Daimon and Roy and about 17.6 % ( $= 15/0.85$ ) in the polymer of the present work.

In Fig. 4, the zeta potential as a function of the polymer or monomer addition is shown. No substantial change in the zeta potential is caused by the monomer independently of the time of addition, whereas a remarkable increase in the zeta potential is recorded in the presence of polymer. So a certain relationship exists between flowability, adsorption on the cement surface and zeta potential. In fact the monomer does not modify flowability of the cement paste (Fig. 1) and at the same time it is adsorbed to a negligible extent on the cement surface (Fig. 2) and causes only insignificant changes in zeta potential (Fig. 4). On the other hand, polymer addition increases flowability

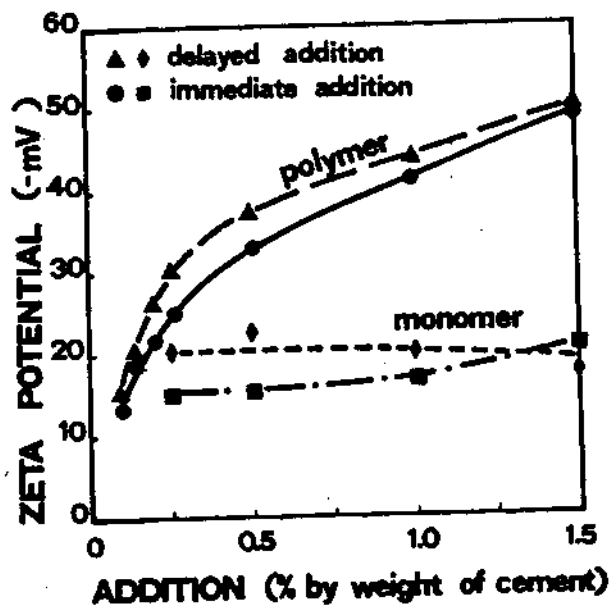


Fig. 4 - Zeta potential as a function of polymer or monomer addition.

(Fig. 1) and zeta potential (Fig. 4) and it is remarkably adsorbed on the cement surface (Fig. 2). This would confirm (6) that the dispersing effect of the superplasticizer is caused mainly by the change in

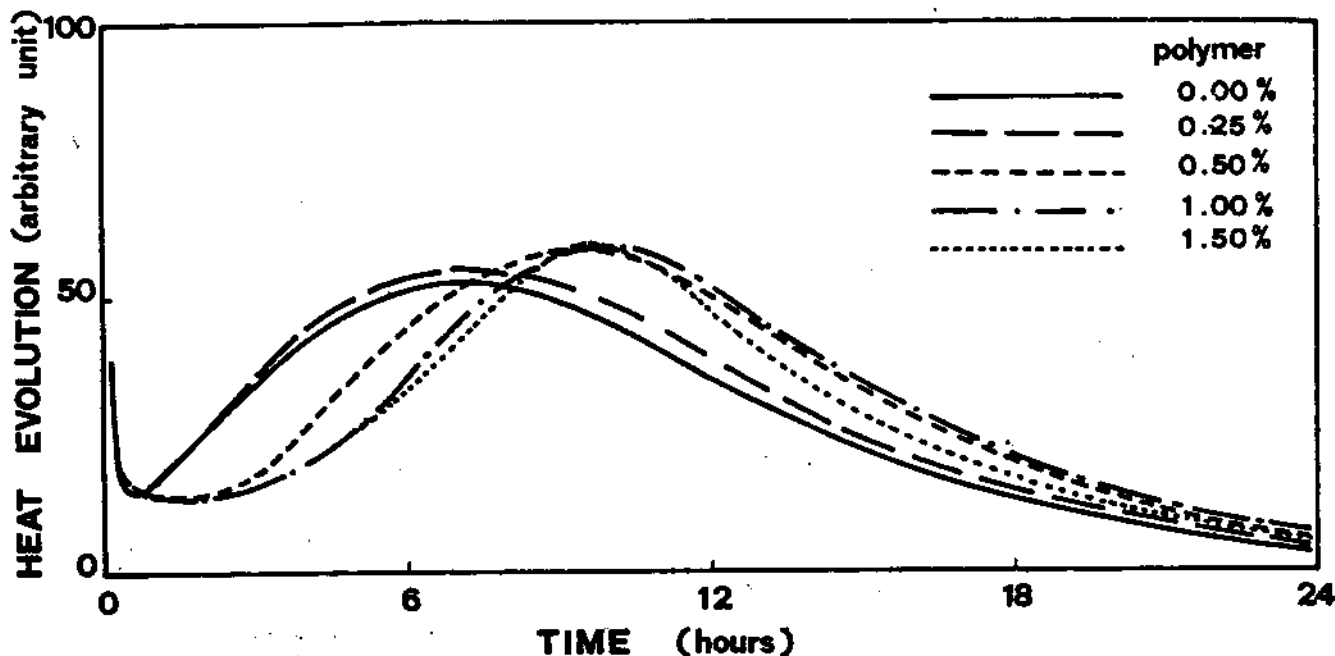


Fig. 5 - Heat evolution rate of cement pastes with different dosage rates of polymer as a function of time.

zeta potential as a function of polymer adsorption on the cement particles. However, some other effect must be taken into account to explain that a delayed polymer addition causes larger increases in flowability and zeta potential, whereas the amount of adsorbed polymer is lower than the one for immediate addition of admixture with mixing water. This would confirm the above mentioned hypothesis that a certain part of the polymer is incorporated within the hydrated product formed during the initial mixing time (2.5 min), so that the effective amount of polymer adsorbed on the hydrated cement surface would be larger in the delayed polymer addition. This seems to be confirmed by the results concerning the polymer addition on the hydration rate, as it is seen further on.

Fig. 5 shows heat evolution rate of the cement in the presence of different amount of polymer added with the mixing water. No substantial change in the heat evolution curve is recorded with a polymer addition of 0.25 %. In the presence of higher amounts of polymer the induction period is proportionally delayed, whereas the hydration rate in the acceleratory period is not substantially changed, so that the time of the heat evolution peak is increased by some hour. With a delayed polymer addition the retarding effect is slightly increased particularly when larger amounts of polymer (0.5 - 1.5 %) are used.

In Fig. 6 the X-ray line at 2.18 Å ( $C_3S + C_2S$ ) is reported as a function of the time for immediate polymer addition. Free calcium hydroxide analysis by DTG confirms that higher dosages of additive (0.5 - 1.5 %) and particularly delayed addition cause a more remarkable retardation in the  $C_3S$  and  $C_2S$  hydration.

Isothermal calorimetry, XRD and DTG show that the monomer (0.25 - 1.5 % by weight of cement) does not change the hydration rate independently of the time of addition.

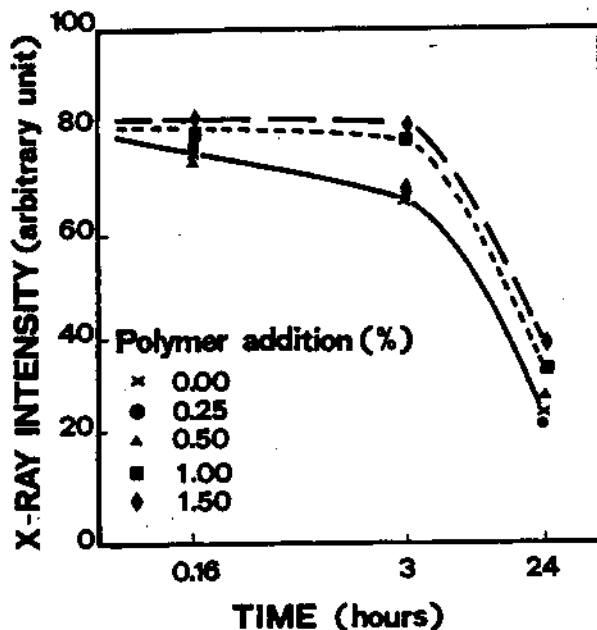


Fig. 6 - X-Ray intensity of cement pastes with immediate addition of different dosage rates of polymer as a function of time.

According Kondo (2) type I anionic surfactants having an hydrophilic group ( $-SO_3Na$ ) at the end of the molecule, when present more than a critical amount, are closely adsorbed on cement particle (Fig. 7a). On the other hand, for type II anionic surfactants, having hydrophilic groups in the molecule, a "flat" adsorption occurs instead of "close" adsorption (Fig. 7b). Kondo found that the hydration of cement was strongly retarded when more type I surfactants were added than a critical amount, while in the case of type II the retarding effect became gradually larger with increasing amount of surfactants. Kondo found that the sulfonated naphthalene monomer is a type I anionic surfactant and its critical amount is about 0.3 - 0.4 % by weight of cement, whereas the sulfonated naphthalene-formaldehyde condensed polymer is a type II anionic

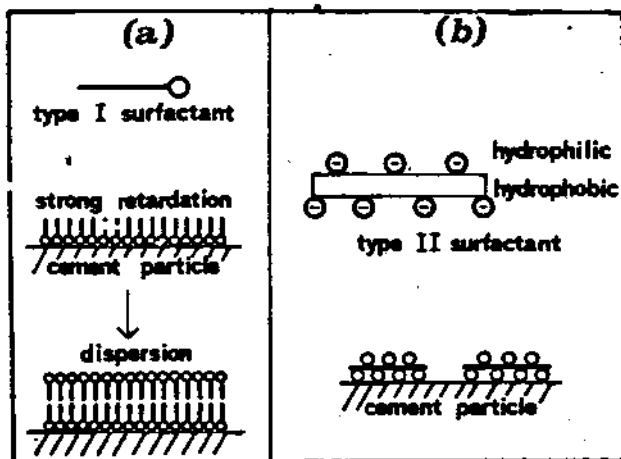


Fig. 7 - Schematic illustration of "close" (a) and "flat" adsorption (b) of anionic surfactants on cement (2).

surfactant. The results of the present paper do not confirm the data of Kondo concerning the behaviour of the monomer, since the cement hydration rate was not changed by monomer addition of 0.25 - 1.50 %. On the other hand no significant adsorption (Fig. 2) or change in the zeta potential (Fig. 4) were recorded. However the authors of the present paper found that the flat polymer adsorption suggested by Kondo is at moment the most convincing mechanism to explain the influence of the polymer on the flowability of fresh mixes.

#### CONCLUSIONS

It seems that there is a certain relationship between the dispersing effect of the admixture and the retarding effect on the cement hydration. Monomer addition neither affects the cement hydration rate nor influences the flowability of the cement paste, while the product is adsorbed on the cement surface to a negligible extent and the zeta potential does not significantly change. On the other hand, polymer addi-

tion increases the flowability of the cement paste and retards the cement hydration rate. It is significantly adsorbed on the cement surface and does change the zeta potential. The effect of the polymer increases by increasing the dosage rate and delaying the addition time. With a dry polymer addition of 0.25 - 0.50% by weight of cement corresponding to that of liquid commercial superplasticizer the dispersing effect is good enough without any significant retarding effect in the hydration rate. With higher dosage rate (1 - 1.5 % of dry polymer by weight of cement), corresponding to three-four times the normal dosage of a liquid commercial superplasticizer, the retarding effect is significantly increased whereas the flowability is not substantially improved.

The results of the present paper would suggest that a certain number of sulfonic groups all linked to a naphthalenic-methylene polymer chain is essential to a flat adsorption (2) and then to an increased dispersing effect.

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