

Dispersing Mechanism of Carboxymethyl Starch as Water-Reducing Agent

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ABSTRACT: In this article, by using zeta (ζ) potential analyzer, X-ray photo spectroscopy, and UV-visible adsorption spectrophotometer, the adsorption characteristics and surface electrochemical properties of carboxymethyl starch (CMS) as water-reducing agent on cement particles and its effects on the fluidity of cement paste were studied in comparison with traditional naphthalene sulfonic acid-formaldehyde condensates, whose dispersion ability mainly depends on electrostatic repulsive force caused by ζ -potential. The

results indicate that the adsorption conformation of CMS is dendritic, generating strong steric hindrance by branched chains and polar side chains of adsorption layer, and the dispersion capacity of CMS mainly comes from steric hindrance effect rather than electrostatic repulsive force. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 486–491, 2007

Key words: dispersing mechanism; carboxymethyl starch; steric hindrance; electrostatic repulsive force

INTRODUCTION

Usage of water-reducing agent is recognized to be the most efficient way to improve the workability of concrete, without increasing the water content.¹ There has been many studies on the working mechanisms of water-reducing agents.^{2–6} It is broadly accepted that water-reducing agents produce dispersion effect through adsorption on cement particles surface, and adsorption characteristics and surface electrochemical properties of water-reducing agents depend on its adsorption conformation and molecular structure.^{7,8} For example, the adsorption conformation of the naphthalene sulfonic acid-formaldehyde condensates (FDN) is lying on the surface of cement particles due to its linear and low-branched molecular structure, and so its dispersion capacity mainly depends on electrostatic repulsive force produced by the adsorption double-electrical layer.⁹ The adsorption conformation of polycarboxylic acid (PC) is comb-type, whereas PC disperses cement particles with the help of the steric hindrance effect that results from the extension of their graft chains away from the surface of cement particles.¹⁰ Therefore, it is important to study how water-reducing agents are adsorbed on the cement particles for controlling rheology of cement paste.

Recently, a new type of water-reducing agent, carboxymethyl starch (CMS), has been synthesized based on starch of low molecular weight.¹¹ This modified polysaccharide was found equal or possess better dispersing properties than that of FDN, but the fact why this substance has superior dispersing capacity is unsolved. This article focused on dispersing mechanism of this new type of water-reducing agent. The effect of FDN and CMS on rheology of cement paste and ζ -potential of cement particle surface as well as their adsorption characteristics were also investigated. The dispersing mechanism of CMS was discussed compared with that of FDN, based on these experimental results.

EXPERIMENTAL

Materials

A commercially manufactured ordinary Portland cement came from Dalian No.3 cement plant in China. National cornstarch with 80% amylopectin (Shenyang Wanshun Starch, Shenyang, China) was used to prepare CMS according to the method of Vieira¹¹ and the degree of substitution of carboxyl was determined by the method of heat paste titration.¹² FDN used in this study was a commercial product. All other reagents were commercially available and were used without further purification.

Analysis of CMS

Fourier transform-infrared (FT-IR) spectra were obtained from KBr pellets of cornstarch and CMS, with a Thermo Nicolet FT-IR Spectrometer (model-Nexus 470FTIR).

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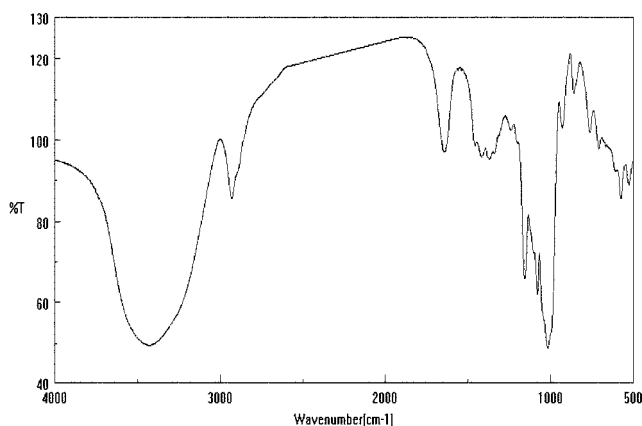


Figure 1 IR spectrum of starch.

The thickness of the adsorbed layer of admixtures on the surface of cement particles was determined by X-ray photo spectroscopy technology (MK II, U.K.). Cement was dipped for 15 min in admixture solutions with concentration of 10 g/mL, with the ratio of water/cement 0.5:1, and then dipped in methyl alcohol to stop hydration. Carbon is a characteristic element that can distinct cement surface from admixture. Hence, adsorption peak strength of C_{1s} on cement surface at different etched depths, before and after adsorption, was measured by using XPS aid of Ar-ion etching analyzer. When peak strength was equal to that of plain cement (before adsorption), the etched depth was considered to be the thickness of the adsorption layer.

GPC (Waters 1525/2414, US) with column (Waters 150c) was used for determination of the molecular weight of CMS. As eluant, the solution of sodium nitrate was used, and the flow rate was 0.8 mL/min. Calibration was carried out with polyethylene glycol (provided by Waters) standards giving an optimum linear function.

ζ -Potential measurement

A certain amount of cement was added to the solution, with certain concentration of water-reducing agent according to a solid/liquid ratio of 0.0025. After mixing for 5 min by blender, the mixture was separated by centrifuge. Then the supernatant was added into electrophoresis pool and analyzed by Zeta potential analyzer (Brookhaven, US). The average of 10 experimental potential data was regarded as ζ -potential of cement particles.

Adsorption amount measurement

CMS showed very weak adsorption within UV-visible region, but it can give an orange-yellow color when treated with phenol and concentrated sulfuric

acid. So the phenol-sulfuric acid method was used to determine the concentration of CMS in solution.¹²

A series of CMS and FDN solutions with different concentrations were prepared. Then cement was added with a solid/liquid ratio of 0.2. After stirring for 10 min, the mixture was separated by centrifuge. The supernatant was colored by phenol-sulfuric acid method, and the concentrations of admixture in the aqueous phase were measured by UV adsorption spectrophotometer (UV-3100, Japan). The quantities adsorbed were calculated from the differences in the concentration of admixtures in the liquid phase before and after adsorption.

$$n^s = \frac{V(C_0 - C)}{m} \quad (1)$$

where n^s is the adsorption capacity (mg/g), C_0 and C are the concentrations (mg/mL) of water-reducing agent before and after adsorption respectively, V is the volume of solutions in milliliters, and m represents the weight of the cement (g).

Fluidity of cement paste

Cement paste was prepared with a water/cement ratio of 0.35. A certain amount of water-reducing agent was added to the mixing water in advance. The fluidity of cement paste was evaluated by pullout spread of a sample from a flow cone specified according to GB8077-87. The maximum diameter of the spread sample and the maximum width perpendicular to that diameter were measured, and the average of these two values was defined as the flow value.

RESULTS AND DISCUSSION

Structure analysis of the CMS

It can be seen from Figures 1 and 2 that IR spectrum of CMS had three new and strong characteristic absorption peaks. The peaks located at 1603 cm^{-1}

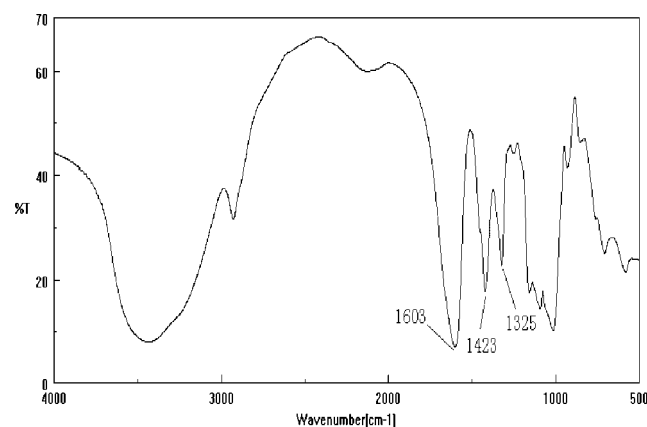


Figure 2 IR spectrum of CMS (DS = 0.51).

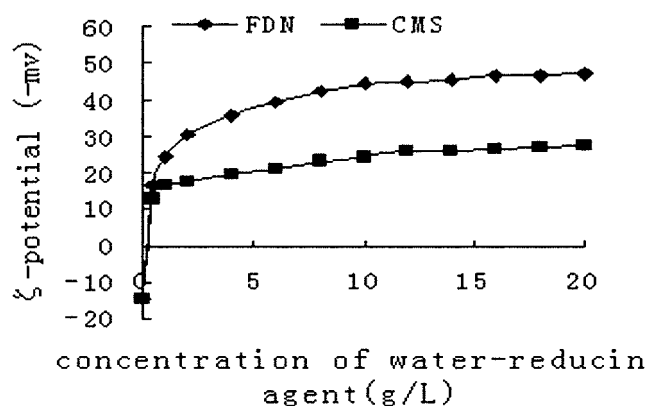


Figure 3 ζ-Potential of water-reducing agents with different concentration.

and 1423 cm^{-1} were characteristic adsorption of C=O and C—O stretching vibration, the peak near 1325 cm^{-1} was attributable to bending stretching of C—H in carboxymethyl, which indicated that the carboxymethyl group was introduced to the corn-starch molecule.

The weight-average molecular weight and the degree of substitution of carboxyl group of CMS were determined to be 1.19×10^6 and 0.51, respectively.

Effect of adsorption of water-reducing agents on the ζ-potential of solid-liquid interface

As shown in Figure 3, the ζ-potential of cement particles was +15 mV in the absence of the admixtures. After addition of anionic surfactants, the adsorption of admixtures changed the charge distribution of double-electrical layer of cement surface, leading to ζ-potential of FDN and CMS changing from +15 mV to -47.21 mV and -27.34 mV, with the concentration of water-reducing agent increasing from 0 to 20 g/L. And the ζ-potential of FDN was higher than that of CMS at the same concentration, which indi-

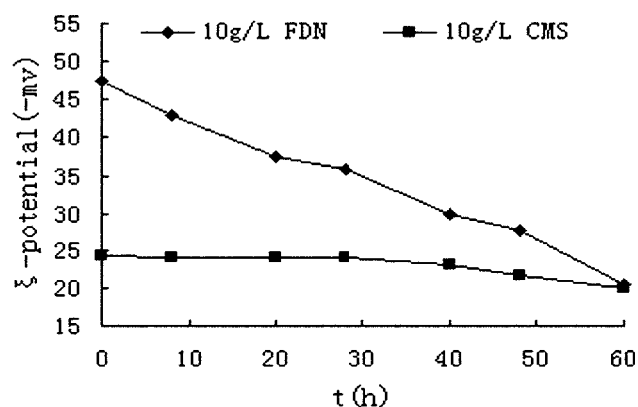


Figure 4 Effect of storing time on ζ-potential of cement particles.

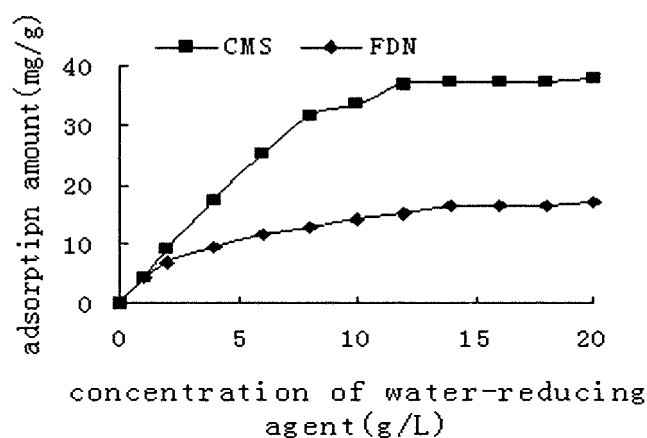


Figure 5 Relationship between concentration and adsorbed amount ($T = 18^\circ\text{C}$).

cated that the electrostatic repulsion force among cement particles adsorbing FDN was higher.

It can be seen from Figure 4 that ζ-potential of FDN and CMS decreased from -50.71 mV to -20.55 mV, and from -26.17 mV to -19.99 mV in 60 h, respectively. So compared with CMS, the FDN adsorbed on the cement particles was easy to be covered by hydration products during the process of hydration.

Adsorption characteristics of water-reducing agents on cement surface

The curve in Figure 5 indicating Langmuir-type adsorption on specific sites was obtained, which could be testified by plotting the reciprocal values of concentration of water-reducing agent and adsorption amount.

Langmuir equation is applied to quantify adsorption capacity and is given as follows:

$$\frac{C_e}{Q} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \quad (2)$$

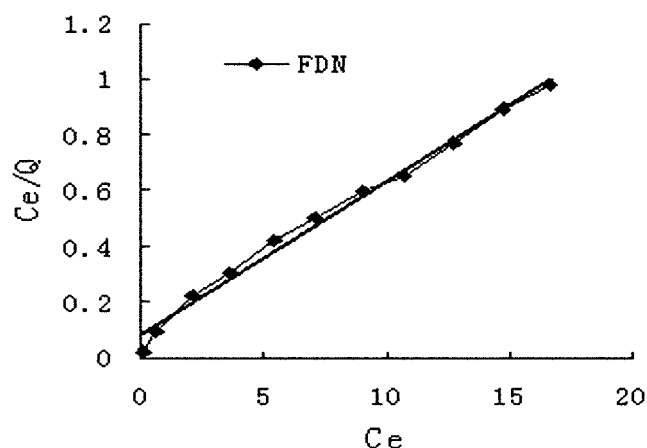


Figure 6 Langmuir adsorption isotherm for the adsorption of FDN on cement particles.

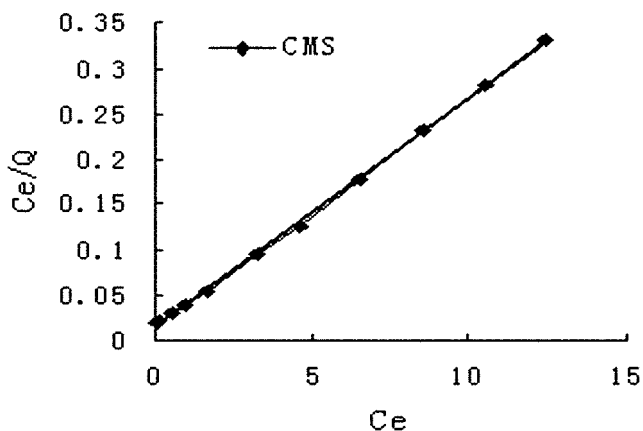


Figure 7 Langmuir adsorption isotherm for the adsorption of CMS on cement particles.

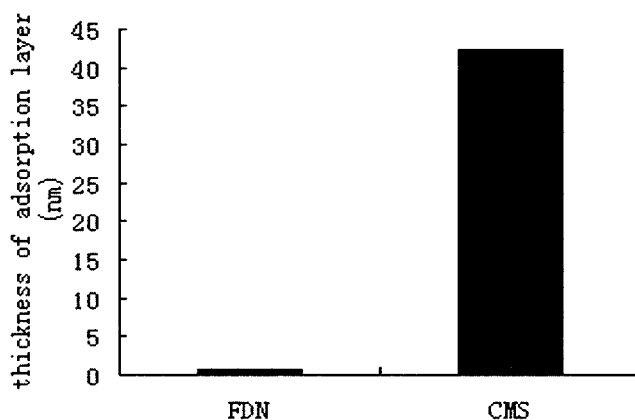


Figure 8 The thickness of adsorption layer of water-reducing agents.

where C_e and Q are equilibrium concentration (g/L) and equilibrium adsorption capacity (mg/g), respectively; Q_m and b are the Langmuir constants representing maximum adsorption capacity (mg/g) and adsorption constant, respectively. The straight lines are given by plotting C_e/Q versus C_e of FDN and CMS in Figures 6 and 7, which give the values of b and Q_m in Table I according to the intercept and slope of these lines, respectively. The maximum adsorption capacities of FDN and CMS are 18.02 and 39.68 mg/g, respectively.

It can be concluded that Langmuir-type adsorption occurred during the process of adsorption of FDN and CMS on cement particles due to their correlation coefficient being close to 1.0.

Figure 8 was shown that the thickness of the adsorption layer of FDN and CMS were 0.58 and 42.2 nm, respectively. Although the adsorption isotherm of FDN and CMS both conformed to Langmuir-type adsorption, the thickness of adsorption layer of CMS was ~73 times of FDN, which indicated that the molecular adsorption state of FDN and CMS on cement particles was quite different.

Effect of water-reducing agents on the fluidity of cement paste

Figures 9 and 10 show the effect of dosage of water-reducing agent on the fluidity and time dependency of fluidity of fresh cement paste, respectively.

TABLE I
Langmuir Parameters for the Adsorption of Water-Reducing Agents on Cement Particles at 18°C

| Water-reducing agent | Q_m (mg/g) | b (L/g) | Correlation coefficient |
|----------------------|--------------|-----------|-------------------------|
| FDN | 18.02 | 0.69 | 0.9905 |
| CMS | 39.68 | 1.75 | 0.9994 |

As can be seen in Figure 9, the water-reducing agent could significantly improve the fluidity of cement paste. The fluidity of CMS and FDN increased from 65 to 257 and 244 mm, respectively, while their dosage increased from 0% to 3.0%. And at the same dosage, the fluidity of CMS was higher than that of FDN, which means that dispersion capacity of CMS was better. By increase of the FDN dosage, the fluidity of cement paste also increased until it reached its maximal adsorption amount of 18 mg/g (dosage was 1.8%). While for CMS, when the adsorption amount of CMS on the surface of cement particles exceeded 8 mg/g (dosage was 0.8%), the fluidity did not increase any more. So compared with FDN, less adsorption amount of CMS could produce more dispersing power among cement particles.

As shown in Figure 10, during the process of hydration, the fluidity of cement paste with FDN reduced by 27.8% (reduced from 265 to 251 mm) in 2 h. Whereas the fluidity loss of cement paste with CMS was just 5.3% (reduced from 194 to 140 mm) in

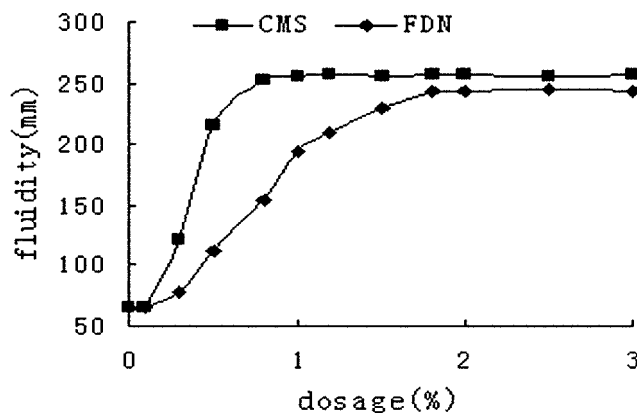


Figure 9 Effect of water-reducing agents addition on the fluidity of cement paste.

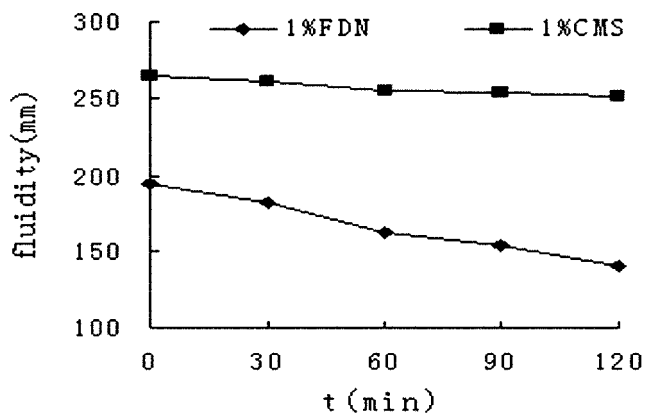


Figure 10 The storing time dependency of the fluidity of cement paste.

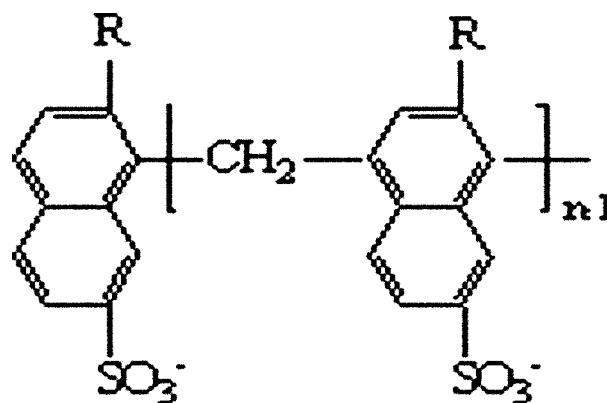


Figure 12 The molecular structure of FDN.

the same time, which indicated that the dispersion stability of CMS was superior to that of FDN.

The molecular structure of FDN and CMS is shown in Figures 11 and 12. It can be seen that the dispersing property of water-reducing agent is closely related to the configuration of the molecule.

The molecular structure of FDN was linear and short-branched, and its molecules lied like rod on the surface of cement particles as shown in Figure 13(b). The adsorption layer thickness of this kind of adsorption state was just 0.35 nm, which contributed little to stereoeffect. Therefore, the dispersing ability of FDN mainly comes from the electrostatic repulsive force. The thickness of adsorption layer was very thin, so that hydration products were easy to overlay the molecules of FDN on the surface of cement particles, resulting in a reduction of ζ -potential and a rapid flow loss of cement paste as a function of time [Fig. 13(c)].

The molecules of CMS take on dendritic structure for many branched and polar side chains.

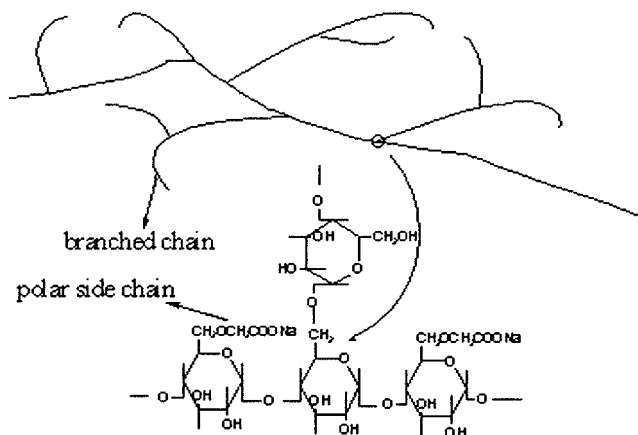


Figure 11 The molecular structure of CMS.

During adsorption, some carboxyl groups of CMS "anchored" on the cement surface by the complex action between the carboxylic group and Ca^{2+} , whereas branched and polar side chains protruded in the liquid phase. The molecules of water-reducing agent molecules appear to be in a spatial distribution at the solid-liquid interface, which impede the agglomeration of cement particles as shown in Figure 14(b). During the progress of hydration, the new hydration products could not shelter the adsorption layer of CMS due to the thick adsorption layer of 42.2 nm, and the uncovered branched and polar side chains could also display its dispersing effect as shown in Figure 14(c). So, steric hindrance is less affected by cement hydration and can keep the dispersion capacity and stability for a relatively long time.

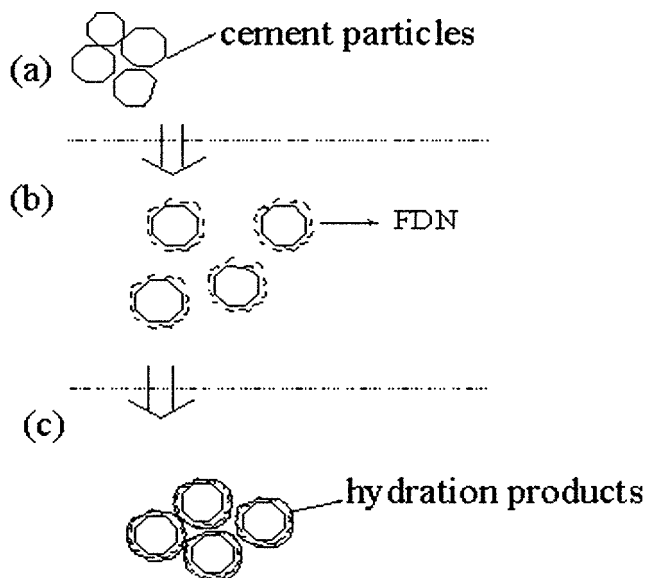


Figure 13 The process of hydration of cement particles absorbing FDN.

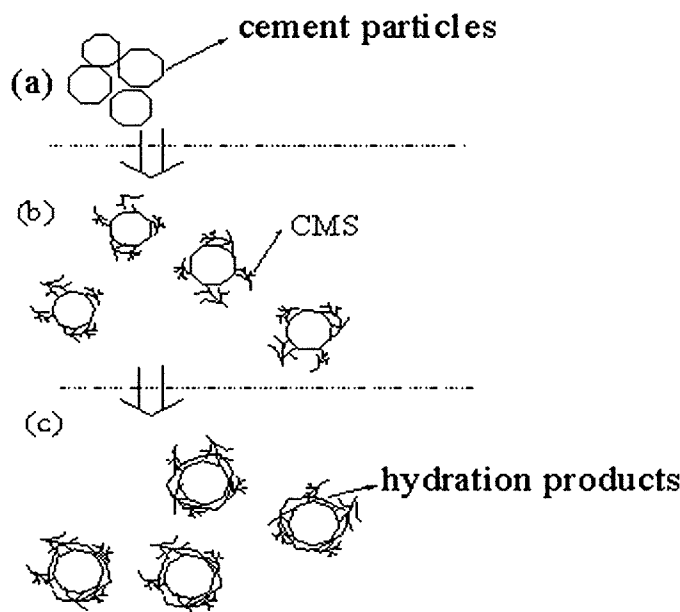


Figure 14 The process of hydration of cement particles absorbing CMS.

CONCLUSIONS

The adsorption of CMS and FDN on cement particles conforms to Langmuir's adsorption isotherm, but the adsorption amount and thickness of adsorption layer of CMS are much higher than that of FDN owing to three-dimensional solid adsorption on the cement particles. Although the ζ -potential of CMS is lower than that of FDN, its dispersion capacity and stability is much better, which indicates that their dispersion mechanism is quite different. The adsorption conformation of CMS is dendritic, generating strong steric hindrance by branch and polar-side chains of adsorption layer, and so its dispersing ability is mainly related with the steric hindrance effect, rather than with the electrostatic repulsive force mechanism. The dispersion of cement particles by steric hindrance is less affected by the rapid hydration of cement; thus, the dispersing stability generated by steric hindrance is much better than that by electrostatic repulsive force and results in little flow loss of fresh cement paste.

References

- Jolicoeur, C.; Simard, M.-A. *Cem Concr Compos* 1998, 20, 87.
- Uchikawa, H.; Hanehara, S.; Sawaki, D. *Cem Concr Res* 1997, 27, 37.
- Matsuhisa, M.; Yamada, K.; Ishimori, M.; Kaneda, Y. *Proc JCI* 1998, 20, 67.
- Yamaguchi, O.; Nakajima, H.; Takahashi, M. *JCA Proc Cem Concr* 1995, 49, 216.
- Hanehara, S.; Yamada, K. *Cem Concr Res* 1999, 29, 1159.
- Yoshioka, K.; Sakai, E.; Daimon, M.; Kitahara, A. *J Am Ceram Soc* 1997, 80, 2667.
- Hsu, K.-C.; Chiu, J.-J.; Chen, S.-D.; Tseng, Y.-C. *Cem Concr Compos* 1999, 21, 425.
- Zhang, T.; Shang, S.; Yin, F.; Aishah, A.; Salmiah, A.; Ooi, T. L. *Cem Concr Res* 2001, 31, 1009.
- Xiuchun, H.; Cuiyu, L.; Baiping, Y. *J Chin Chem Soc* 1986, 14, 392.
- Sakai, E.; Kang, J. K.; Daimon, M. *Abstracts of Papers, Sixth CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Nice, France, October 2000*.
- Vieira, M. C.; Klemm, D.; Einfeldt, L. *Cem Concr Res* 2005, 35, 883.
- Lu, Y.; Lu, G. *Hunan Chem Ind* 1999, 4, 40.
- Dubois, M.; Gilles, K. A.; Hamilton, J. K. *Anal Chem* 1956, 28, 350.