2.2.6 Effect of chemical admixture on hydration

By addition of admixtures, the hydration of Portland cement in the first hours is retarded depending upon the type and dosage of admixtures. Figure 2.2.6.1 depicts the delay in hydration of cement C due to the addition of a polycarboxylate based admixture. The peak in blank mix (no admixture) is reached after approx. 7 hours, whereas the peak in the PC mix is reached after approx. 9 hours.

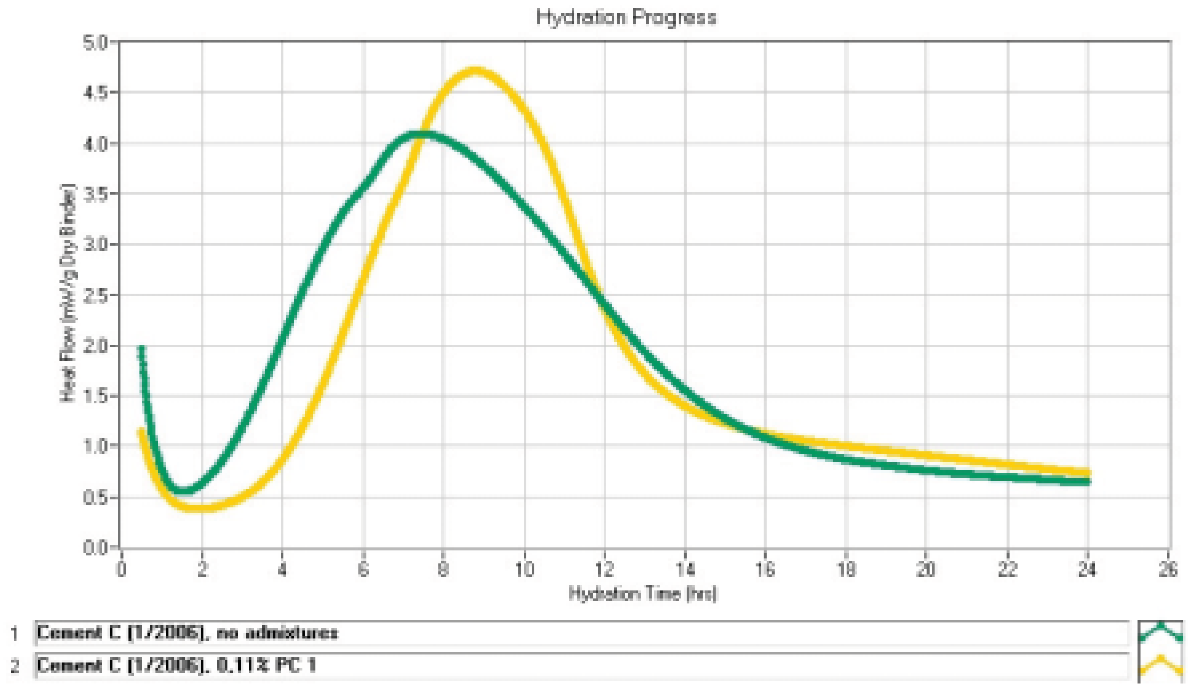

Figure 2.2.6.1: Hydration curve of cement C (blank and PC mix)

Uchikawa et al. /Uc 1/ have investigated the effect of different kind of admixture on cement hydration. The admixtures used were polycarboxylic acid-based, lignin sulfonic acid-based and other products. The heat evolution curves showed that the hydration was delayed by any admixture. Depending upon the timing of addition (simultaneous or later addition of admixtures) the retardation of hydration process was between 1 and 12 hours. Later addition resulted in a clearly longer retardation. The polycarboxylic based admixture caused the strongest retardation of all four admixtures used in the study. The retarding effect of all admixtures was indirectly related to the higher adsorption rates of the polymers on the aluminate phase than on the alite phase /Uc 1/.

Cerulli et al. have reported about a new type of polycarboxylate superplasticizer, developed for utilization in cold climates. The authors saw a need for this type of superplasticizer due to the sometimes strong retarding effect of polycarboxylate polymers on cement hydration. /Ce 1/ This disadvantage of polycarboxylate polymers can limit the use of these superplasticizers in cold climates (e.g. Iceland), particularly in the cases where early strength development is required /Ce 1/. The new polycarboxylate superplasticizer, characterized by a completely different molecular structure in comparison with the traditional ones, gave sufficient strength development in cold climates. The authors believe that the characteristics of the new superplasticizer seem to be ascribed to its capacity to modify the morphological structure of ettringite formed in the first period of hydration /Ce 1/.

2.3 Dispersing mechanisms in cementitious systems

Plasticizers and superplasticizers for concrete act by adsorption at the solid-liquid interface between the particles and the aqueous phase. After adsorption, repulsive forces between the superplasticizer polymers lead to the dispersion of the cement grains. For sufficient workability of a cementitious system (i.e. concrete), the repulsive forces have to be stronger than the adhesion forces (van der Waals or electrostatic forces) between the colloidal particles. Without superplasticizer, the colloidal cement grains would flocculate and reduce the workability of the mix /Tay1/.

2.3.1 Colloidal particles

The particle size distribution of cement is varying from micrometres (10^{-6} m) to nanometres (10^{-9} m). Therefore, cement is, at least partly, a colloidal system. Although the amount of particles smaller than 1 µm is only in a range of 8 to 10 % (by weight), these particles are very important from rheological point of view. The small particles, responsible for the high specific surface, are the place where the polymers act as dispersing admixtures. Shaw et al. /Sh 1/ summarized the factors which contribute most to the overall nature of a colloidal system like cement as following:

- Particle size
- Particle shape and flexibility
- Surface properties (including electrical ones)
- Particle-particle interactions
- Particle-solvent interactions

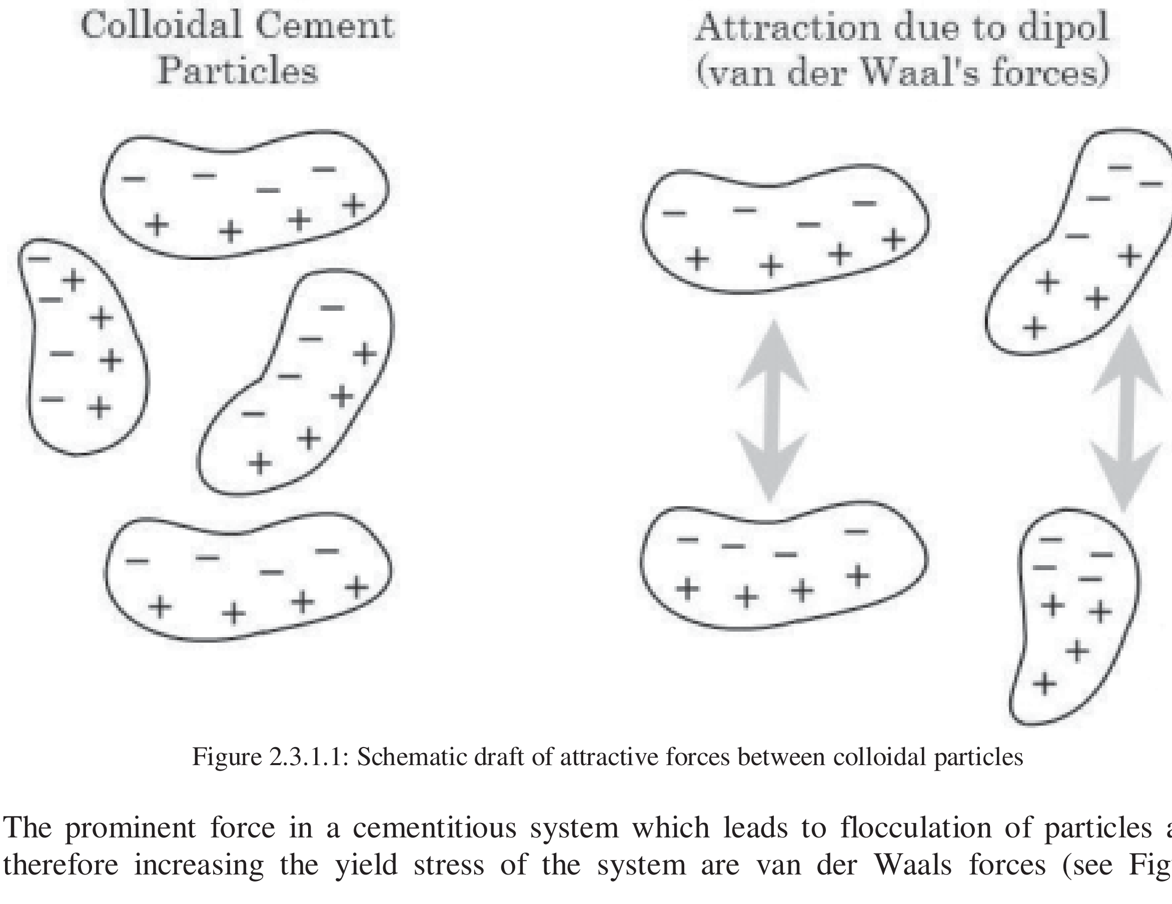

Figure 2.3.1.1: Schematic draft of attractive forces between colloidal particles

The prominent force in a cementitious system which leads to flocculation of particles and therefore increasing the yield stress of the system are van der Waals forces (see Figure

2.3.1.1). These are forces of attraction due to the particles having dipoles. Particles with dipoles have a distribution of electrons such that the electron density is higher at one end than the other. These forces are only active in the immediate vicinity of the particles and are of great importance particularly for small particles. In other words, the distribution of electrons on the surface has a greater influence on the particle-particle interaction than e.g. the g-force on the particle. To control the interactions between colloidal particles, polymeric stabilization has been widely used, especially when the dispersions are subject to harsh processing conditions where the temperature and ionic strength are not constant. Cementitious systems show a rapid increase in ionic strength as ions are released from the cement particle surfaces and a rise in temperature as the hydration reaction progresses between cement particles /Ko 1/.

2.3.2 Electrostatic stabilisation

The more traditional products like lignosulfonate, naphthalene and melamine based superplasticizers disperse the cement particles through a mechanism of electrostatic repulsion. The polymers are adsorbed on the surface of the cement particles, giving them a negative charge so that they repel each other (see Figure 2.3.2.1). This charge is the so-called zeta potential. It describes the cement particles ability to affect other charged cement particles in the suspension. Observations indicate that the absolute zeta potential of ordinary Portland cement particles with naphthalene- or melamine-type superplasticizers must be more than 20 mV /Li 1/. Thereby, yield stress and viscosity is reduced. After a certain time fluidity is lost again, primarily due to the increase in the ionic strength of the cementitious system, which leads to re-flocculation driven by van der Waals attraction. Since the strong polyelectrolytes (i.e. melamine) do not provide significant steric repulsion (see 2.3.3) to prevent this re-flocculation, copolymers such as weak or grafted polyelectrolytes have been developed to provide both electrostatic and steric stabilization in a single molecular species /Ko 1/.

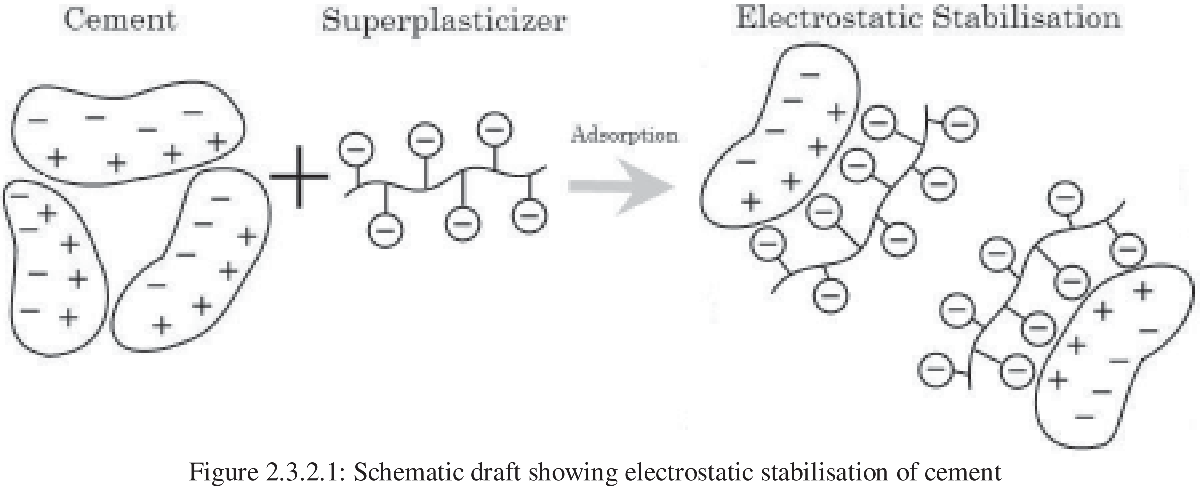

Figure 2.3.2.1: Schematic draft showing electrostatic stabilisation of cement

The primary factor influencing the dispersing effect of admixtures working on the basis of electrostatic stabilisation seems to be the ionic strength of the pore solution. During the hydration process, numerous ions are dissolved and then the so-called pore solution becomes far from an ideal electrolyte. The interparticle interaction forces are strongly influenced by the ionic composition of the pore solution /Ho 1/. In practice, admixtures based on electrostatic stabilisation can provide sufficient workability of concrete for a period of 30 to 60 minutes. The relatively fast workability loss in presence of lignosulfonate, naphthalene and melamine based admixtures can be related to the increase of the ionic strength of the suspending medium, which compresses the adsorbed polyelectrolyte layers and weakens the electrostatic repulsion. As a result, van der Waals attraction leads to re-flocculation of the cement particles /Ho 1/.

2.3.3 Steric hindrance

The dispersing effect of plasticizers from the newer generation like polycarboxylate ether is based on a combination of steric hindrance and electrostatic stabilisation /Ho 1/. Comb type polymers have carboxylic groups in the main chain and comb-type superplasticizers are adsorbed on to cement particles /Ta 2 and Sa 1/. Carboxylic groups of comb-type superplasticizers are coupled with Ca^{2+} ions on the surface of cement particles or hydrated products /Sa 3/. The side chains prevent the particles from coming closer to each other, so that no van der Waals forces can act (see Figure 2.3.3.1). Hence the effect can be seen as a combination of steric and electrostatic repulsion.
According to /Yo 1/, /Uc 1/ and /Uc 3/, the absolute zeta potential (negative charge induced by admixtures) of ordinary Portland cement particles with polycarboxylate based superplasticizers is less than -10 mV. Sakai et al. /Sa 3/ report values between -0,3 and -5 mV for comb type admixtures. This is significantly less than with electrostatic stabilisation. Hence, most of the dispersing effect with comb-type polymers is due to the steric separation provided by the side chains.

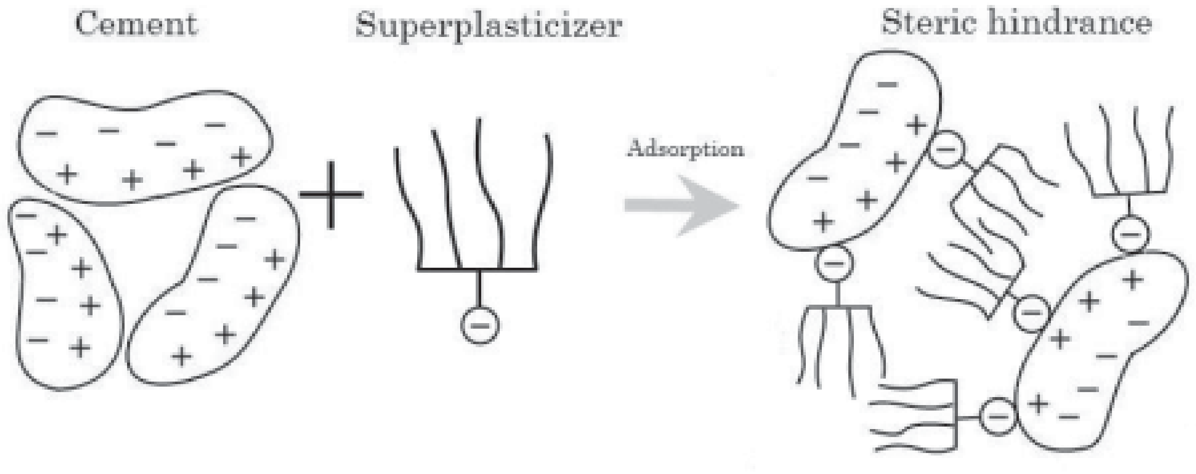

Figure 2.3.3.1: Schematic draft showing stablisation by steric hindrance

The key parameters, which govern the steric repulsion, are the adsorption layer thickness and its conformation at the solid liquid interface /Ho 1/. The effects of the chemical structure on the properties of polycarboxylate-type superplasticizer have been investigated by Yamada et al. /Ya 1/. The parameters evaluated were the polyoxyethylene (PEO) side chain length, the degree of backbone polymerization, the composition of functional groups such as carboxylic and sulfonic groups, and the purity of polymers. Rheological measurements were done on mixes with several w/c-ratios. Among others, the authors found that with decreasing w/c-ratio the chemical structure of the polymers becomes significant. Polymers with longer PEO side chains, lower degrees of backbone polymerization, and higher contents of sulfonic groups showed higher dispersing power /Ya 1/.

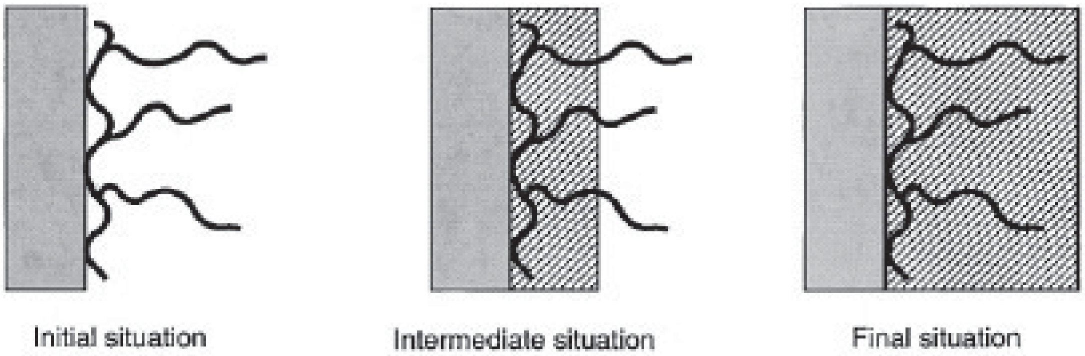

Figure 2.3.3.2: Schematic draft which shows how comb polymers with polyethylene side chains are incorporated by growing hydration layers /Fl 1 and Sa 1/

In practice, admixtures based on steric hindrance can provide sufficient workability for a concrete mix over a period of 60 to 90 minutes. The increase in workability is due to steric hindrance provided by the side chains. According to Sakai et al. /Sa 1/ workability is lost when the hydration layers growing from the surface have incorporated the polymers (see also Figure 2.3.3.2).

2.3.4 Adsorption of polymers on cement surface

Plank et al. /Pl 1/ investigated the zeta potential of early hydration products and found it to be a key factor for superplasticizer adsorption. The authors conclude that the adsorbed amount of superplasticizer strongly depends on the existence of a positive zeta potential of the hydration phase /Pl 1/. (1) Therefore, ettringite (due to its positive charge) is able to adsorb high quantities of negatively charged superplasticizers. Mineral phases with a zeta potential around zero or even a negative zeta potential do not adsorb significant amounts of superplasticizers. (2) High surface area by itself does not lead to adsorption if the zeta potential is negative or only slightly positive. Thus, a positive zeta potential is a key factor for adsorption /Pl 1/. (3) At comparable specific surface area, ettringite shows 2-4 times more polymer adsorbed per surface area than monosulfate. (4) Another finding was that the adsorbed amount of polycondensates (in mg/g or mg/m²) is much higher than for polycarboxylates (approx. 20 vs. 3-5 mg/m² on ettringite) /Pl 1/. (5) The adsorption ratio of polycarboxylates also depends on their anionic charge density: the higher this charge density, the stronger the adsorption /Pl 1/. Plank et al. conclude that a hydrating grain is best represented by a mosaic structure (see Figure 2.3.4.1), with superplasticizer molecules mainly adsorbed on ettringite (see Figure 2.3.4.1) and some on monosulfate and C-S-H nucleated at surface /Pl 1/.

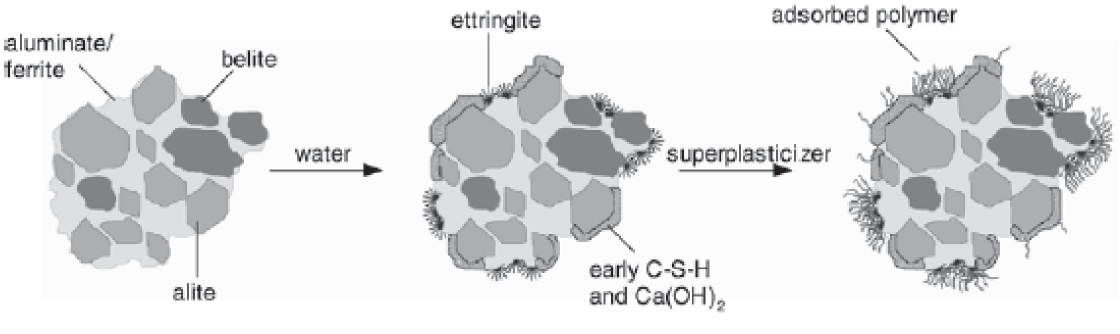

Figure 2.3.4.1: Schematic representation of the cross section of a hydrating cement grain showing uneven polymer distribution on its surface /Pl 1/

Yoshioka et al. /Yo 2/ investigated the adsorption characteristics of various superplasticizers on Portland cement component minerals. Adsorption isotherms of various types of superplasticizers and zeta potentials of cement component materials at the maximum adsorption of the superplasticizers were measured /Yo 2/. The authors found that for all types of superplasticizers, a larger amount of superplasticizer was adsorbed on C_3A and C_4AF than C_3S and C_2S. Without superplasticizer, C_3S and C_2S had negative zeta potential (around -5 mV). On the contrary, C_3A and C_4AF had positive zeta potential (in the range of +5 to +10 mV). Figure 2.3.4.2 depicts the zeta potential of each mineralogical composition of cement in a solution with and without superplasticizer. Yoshioka et al. concluded that accelerated coagulation of cement particles in a paste with no admixtures might occur due to this opposite charge in particles /Yo 2/. Another finding was that all mineralogical components of cement showed negative zeta potential when they are dispersed in a solution with superplasticizer.

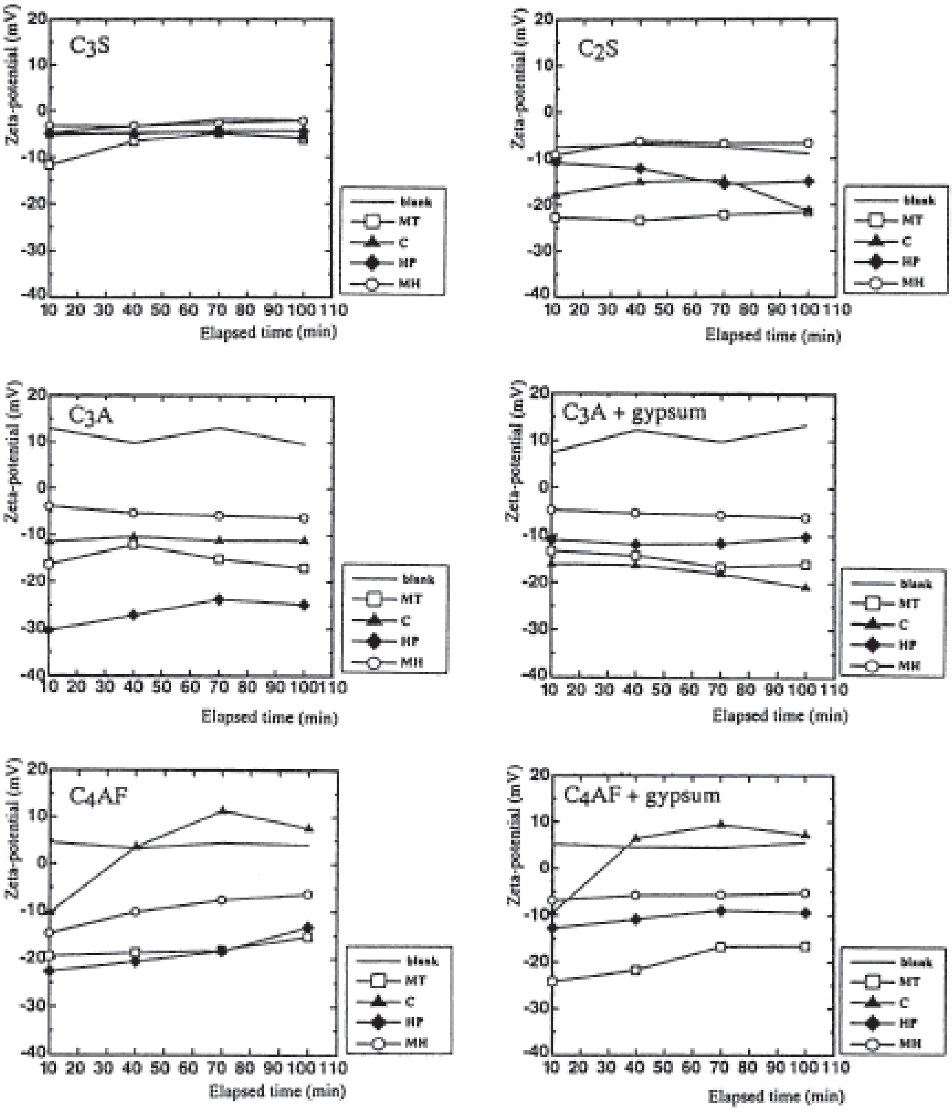

Figure 2.3.4.2: The zeta potentials of each mineralogical composition of cement in a solution with and without superplasticizer /Yo 2/

2.4 Interaction between cement and admixture

Flatt et al. /Fl 1/ have given a simplified view on the chemical effects perturbing the action of superplasticizers. The authors proposed three categories which describe the interactions and state of superplasticizers with the cement suspensions. According to their model, the first part of polymers is consumed by intercalation, coprecipitation or micellization, i.e., by formation of an organo-mineral phase (OMP). A second part of the polymer is adsorbed onto the surface of particles and helps disperse cement agglomerates. The third part consists of the excess superplasticizer neither consumed nor adsorbed and which remains dissolved in the aqueous phase /Fl 1/. In the conclusion the authors state that, at equal dosage, a cement with a larger degree of consumption (due to formation of OMP) can have a lower surface coverage and consequently poorer workability. The authors specifically highlight the difference between the consumption of polymers and the adsorption of polymers on the clinker surface /Fl 1/. The intercalation of polycarboxylates into C_3A phases was also reported by Plank et al. /Pl 2/.

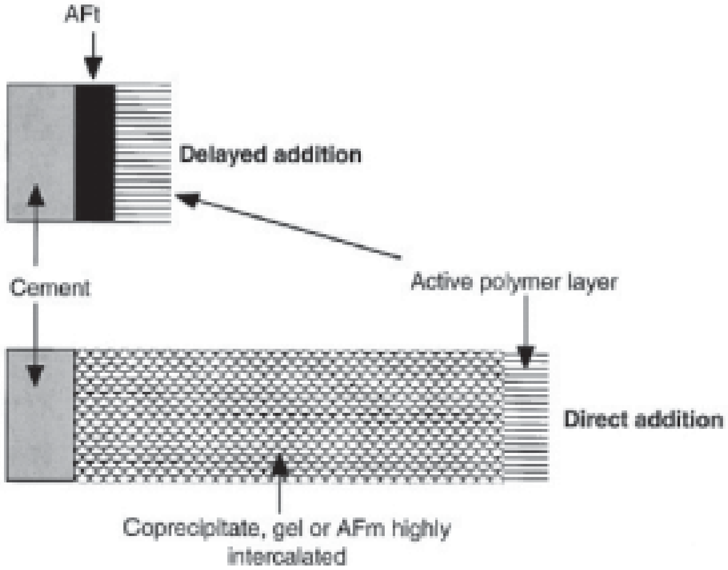

Figure 2.4.1: Schematic illustration of OMP precipitation /Fl 1/

Figure 2.4.1 shows the chemical sink effect of OMP precipitation. In the case of direct addition, many polymers are consumed uselessly. The plane of action for the van der Waals force would be shifted from the surface towards the base of the polymer /Fl 1/.

An important factor with regards to cement-admixture interaction is the timing of addition of the dispersing admixture. Uchikawa et al. /Uc 1/ have shown the effect of simultaneous (with water) and delayed (after water) addition for four kinds of organic admixtures on composition, structure and property of fresh cement paste. It was found that the flowability of cement paste produced by later addition of any admixture was higher than that of cement paste produced by simultaneous addition /Uc 1/. It was also found that any admixture is more adsorbed on the aluminate phase than on the alite phase. By later addition, the adsorption of admixtures on the clinker surface (in particular on C_3A) is reduced, leading to an improvement of fluidity /Uc 1/.

Cement admixture interaction problems, which are well-known by concrete producers, were investigated by Hanehara et al. /Ha 1/. The problems reported from practice range from variation of initial slump to large slump loss during concrete production and placement /Ha 1/. Normal Portland cements coming from four different plants were tested with different types of admixtures. The chemical admixtures were based on lignin sulfonate, naphthalene sulfonate, melamine sulfonate, amino sulfonate and polycarboxylate ether. Several interaction problems were observed during this research, which were classified in two groups. (1) Problems caused by the effect of the admixture´s addition on the hydration reaction of cement, and (2) problems caused by the adsorption of the admixture on the cement particles /Ha 1/. The authors state that the rheology (flow values) of the four types of cement paste prepared without admixtures is almost identical, while those prepared with admixtures fluctuated highly. The authors also observed an important influence of addition time on fluidity of paste. In case of polycarboxylic acid-based admixture, the major influencing factor on fluidity was found to be the amount of alkaline sulphates in cement /Ha 1/.

In /Ze 1/ the development, trial tests and production of a nuclear shielding concrete is described. The task here was to develop a concrete with a high slag content cement (CEM III/A 32,5) and high density materials. The concrete should show sufficient workability for 60 minutes and segregate not too much. During the trial tests many admixtures of traditional and co-polymer type were tested. Finally, only one polycarboxylate based admixture met the requirements, although the polycarboxylate based admixtures were added at the same dosage or even higher. According to the authors, fluctuations in workability due to type of admixture are considerable.

Bedard et al. give a brief overview of admixture-cement incompatibilities. The authors highlight cases of early stiffening and undesirable retardation of the setting time caused by admixtures /Be 1/. Early stiffening has been found to be caused by changes in the rate of reaction between C_3A and sulphate of the cement. Retardation is found to result from an overdose of admixtures which leads to delayed calcium silicate hydration /Be 1/. With regards to rheology, the authors give examples of cement-superplasticizer incompatibilities in high-performance concrete. The incompatibilities mentioned are: low fluidification effect, rapid slump loss, severe segregation, loss of entrained air and extended set retardation. It was found that the cement superplasticizer (SP) incompatibility problems are magnified in high-performance concrete because of the much reduced water/cement ratios and the higher superplasticizer doses. The authors state that the principal cement and admixture factors influencing rheological behaviour in HPC-SP systems are related to the cement´s C_3A content, Blaine fineness, solubility of the gypsum, and composition of the cement /Be 1/.

Further, it is shown how a low fluidification effect can finally lead to severe segregation of the mix. This can happen when larger dosages of the admixture are added to offset the lack of initial fluidizing of the concrete or to reinstate workability (e.g. after rapid slump loss). Thereby, the saturation point for the admixture can be exceeded easily. At this point one can use the well-known trick from practice to save a segregating concrete. The authors recommend addition of extra quantities of cement to the mix to consume the excess admixture. Extended retardation of mixes containing SP is found to be closely related to Blaine surface, chemical composition (mainly C_3A content) of the cement, SP dosage and concrete temperatures. With equal dosage of SP, cements with lower C_3A content are retarded considerably more than cements with higher C_3A content /Be 1/.

Zingg et al. /Zi 1/ investigated the micro structural development of fresh cement pastes without and with polycarboxylate-type (PCE) of superplasticizers by use of cryo-FIB and cryo-SEM techniques. During the investigations, the natural structure of fresh cement pastes was preserved by high pressure freezing. The authors found that in absence of PCE, early hydrates (ettringite) tend to precipitate on clinker surfaces and tend to form agglomerates, which will lead to interlocking bridges and thus, to higher yield stresses at later hydration times /Zi 1/. The interstitial pore space in cement pastes without PCE is almost free of smallest hydrate particles. In contrast, in presence of PCE, the hydrates (mainly ettringite) are well dispersed in the interstitial pore space and only minor amounts are attached on the clinker surfaces. With PCE, almost no agglomerates are formed during the first minutes of hydration /Zi 1/.

Tagnit-Hamou and Aitcin /Tag 1/ summarize some cases of cement-superplasticizer incompatibility which were reported in the literature. Most cases could be explained by variations in sulphate solubility and fluctuations in the sulphate carrier composition /Tag 1/.