ABSTRACT

In this work the rheological behavior (i.e. the flow behavior) of three superplasticizers (polymelamine sulfonate, polynaphthalene sulfonate, polyacrylate) in combination with various Swiss cements (CEM I 42.5) was studied intensively. The aim was on the one hand to determine the interactions between cements and superplasticizers and on the other hand to determine the most important parameters, which influence the rheological behavior during the first two hours of cement hydration. During this time concrete is usually mixed, transported, and placed. The rheological investigations on cement paste, mortar and concrete were completed by XRD, pore water analyses, heat of hydration and DSC-measurements.

The hydration of cement contains many reactions, which mainly depend on the cement composition, the w/c ratio, and on temperature. Both the flow behavior of mortar and concrete at the beginning of the hydration, and the hardening of the cement (or the concrete) are decisively influenced by these hydration reactions. Nowadays, various chemical additives are used, which deliberately or non-deliberately alter the hydration process. Due to the complexity of the ongoing hydration reactions and due to the insufficient knowledge, it is not always possible to alter the hydration behavior as requested.

The most important parameters turned out to be:

- **the amount of C_3A**
- **the water-soluble alkalis (Na^+, K^+)**
- **the type and amount of superplasticizer used**
- **the mortar or cement paste temperature**
- **the w/c ratio**

To date, the influence of temperature has hardly been described. However, in practice, concrete temperature may easily vary from 5 to 30°C.

The content of C_3A and water-soluble alkalis depends on the cement. For the investigated cements these contents vary from 1.5 to 12.6 wt.-% C_3A, and from 0.22 to 0.96 wt.-% Na_2O-eq_{sol}. The influence of these two parameters can only be compared with different cements or simulated by the addition of similar materials. This kind of simulation was done for the water-soluble alkalis by adding Na_2SO_4 to the mixing water.

Pore water analyses showed that the amount of adsorbed and incorporated superplasticizer strongly depends on the C_3A content of the cement. Moreover, this amount was different at equal superplasticizer dosages for the three superplasticizers under study. For the PC superplasticizer it was lowest, whereas for the PNS superplasticizer it was highest. The addition of Na_2SO_4 to the mixing water increased the fraction, which remained in the pore water, i.e. which was not adsorbed or incorporated.

It was shown that the content of SO_3 in the clinker correlates with the water-soluble alkali content (r^2=0.81). It follows that the content of SO_3 in the clinker mainly derives from easily soluble alkali sulfates. Moreover, it was shown that during the first 30 minutes water-soluble alkalis get dissolved by more than 50% and 66% having w/c ratios of 0.35 and 50, respectively. At this time only some percent of the cement has been hydrated. In order to reach such a high dissolved amount, **alkali sulfates preferentially have to be monomineralic and/or they preferentially have to occur at the surface of the polymineralic cement particles. These findings corroborate that besides the addition of calcium sulfates as set retarders, water-soluble alkalis are very important sulfate ion suppliers, especially at low w/c ratios.** This is especially important for the understanding of cement-superplasticizer interactions, since sulfate ions and C_3A are mainly responsible for the adsorption behavior of superplasticizers.

The rheological investigations on cement paste and mortar were performed with a rotational viscometer at constant mortar temperatures (8, 20, 30°C). Thus, the influence of cement paste and mortar temperature on the flow behavior could be investigated. Within the measuring range of the viscometer, the cement suspensions behaved like Bingham-fluids. From the three investigated parameters (relative yield value, relative viscosity coefficient and stiffening value) relative yield value was found to be the most suitable parameter to predict the flow behavior. Without the use of superplasticizers, relative yield value increased with increasing temperature. A possible explanation for this behavior could be the ettringite content, which increased for the investigated samples from 10 to 30°C.

Without the use of superplasticizer the relative yield value of the 10 cements under study was linearly correlated with the product of C_3A times cement fineness (r^2=0.65). If the C_2S content was further considered, the correlation coefficient increased to 0.74. **For superplasticized mortars the quality of the correlation depended on the superplasticizer dosage.** Besides the product of C_3A times cement fineness, no other

parameter could be found. The C_2S content did not have any influence on the correlation coefficient.

By increasing the superplasticizer content the relative yield value decreases. The fluidifying effect of the PC superplasticizer was most pronounced. The impact of Na_2SO_4 addition to the mixing water of superplasticized concrete depended on the investigated systems (i.e. cement-superplasticizer-temperature). **It can generally be assumed that the relative yield value has a minimal value at an appointed Na_2SO_4 content (parabolic curve). At higher or lower contents of Na_2SO_4 the amount is not optimized with respect to relative yield value (concept of the over- and underdosed state with regard to Na_2SO_4 addition). The optimal Na_2SO_4 content can significantly be shifted depending on the superplasticizer and cement used as well as on the mortar temperature applied.** It is thus possible that with an increasing amount of Na_2SO_4 only the increasing part of the parabolic curve is measured.

The influence of Na_2SO_4 addition on the relative yield value could be explained on the basis of a superplasticizer adsorption model. Thereby, fluidity is determined by the amount of superplasticizer adsorbed at the cement particle surface. This amount is influenced by the C_3A content of cement, by the superplasticizer molecules incorporated in the hydrates, and by the content of sulfate ions in the pore water.

The influence of temperature on superplasticized mortars was very variable and not comparable to systems without superplasticizer. Nevertheless, **the temperature characteristics of the relative yield value from 4 of the 5 investigated cements (Cement A, C, D, E) could be explained by the above-mentioned superplasticizer adsorption model, except for cement B.** With increasing temperature a cement-superplasticizer system is changing either into the direction of the underdosed state or into the overdosed one. It seems that the direction of this shift only depends on the cement used. It is independent from the superplasticizer used.

Finally, recommendations of practical interest as well as an outlook on continuative investigations are given.