

Influence of Hydration on the Fluidity of Normal Portland Cement Pastes

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Abstract

The rheological properties of cement paste in dependence on variation of cement characteristics (chemical and physical properties) are widely discussed in literature. Only a few studies show how the cement hydration products influence the fluidity of the pastes. Results presented here contribute to a better understanding of cement hydration and fluidity.

To induce the formation of certain hydration products we systematically modified the cement composition by adding alkali sulphates. Furthermore results of rheology, phase analysis and microstructural investigations were combined in order to reveal the influence of hydration products on the fluidity of the cement paste.

Thereby it is shown how the growth of long prismatic crystals like syngenite decreases paste fluidity. The increase in fluidity during continuous stirring is attributed to microstructural changes.

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1 Introduction

Workability of concrete is of great importance for realisation of modern building projects. Admixtures like superplasticizers are applied to modify the concrete flow characteristics. Many investigations have been carried out on the influence of superplasticizers on cement and concrete performance. But the basic understanding of rheological behaviour and setting of cement paste is still being discussed.

Results of microstructural and phase composition analysis showed that normal setting is related to alite hydration and it starts during the acceleratory stage of hydration [1-4]. Microstructural investigations by ESEM indicate that the interlocking of the nanostructured C-S-H phases leads to setting of cement paste [5]. However, other investigations suggest that setting is the result of particle agglomeration driven by cohesion forces [6].

Contrary to normal set, undesired (early) set of cement paste is caused by crystallisation of AFm phases (flash set) or gypsum and syngenite (false set). Flash set is indicated by an increased release of hydration heat [1, 3].

The rheological behaviour of normal Portland cement pastes is explained by several different mechanisms: Powers [7] introduced the model of agglomerating / flocculating cement particles. Driving forces for agglomeration / adhesion of cement particles are van der Waals forces, electrostatic forces and hydration forces [7-10]. Recently Flatt et al. [11] and Kauppi et al. [12] tried to model and to measure these forces with the aim to predict plastic viscosity and yield stress of cement paste [13].

Other investigations [14-19] showed the dependence of rheological properties of cement pastes on cement and hydration characteristics (specific surface area of cement, clinker and set regulator reactivity etc.). Several authors [15, 20] suggested that formation of short prismatic ettringite increases the interparticle interaction and this leads to an increased viscosity of the cement paste.

To better understand how the formation of hydration products influences the fluidity of the cement paste we qualitatively and quantitatively characterised cement hydration, microstructure and changes in specific surface area of cement. Obtained results were compared with fluidity measurements. On this basis we have been able to evaluate the influence of hydration products like syngenite on the fluidity of cement pastes. Exemplary studies on concrete fluidity have been carried out to determine if an increased quantity of syngenite crystals in cement paste influences concrete rheology.

2 Materials and methods

2.1 Cements

Two commercial cements of type CEM I 42.5 R (CEM A) and CEM I 52.5 R (CEM B) according to European Standard DIN EN 197-1 were used. Chemical composition of studied cements is given in Table 1.

Table 1 – Chemical composition of cements (wt.%, ws = water soluble).

CEM	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	K ₂ O _{ws}	Na ₂ O _{ws}	SO ₃	MgO
A	63.2	20.3	6.0	3.1	0.55	0.11	0.32	0.04	2.8	1.1
B	66.0	22.9	4.0	1.3	0.66	0.23	0.40	0.06	3.1	0.6

Potassium and sodium sulphate were added to the mixing water in order to increase the amount of soluble alkali in the commercial cements. By assuming that all water soluble potassium is bound to sulphate CEM A contains 0.6 wt.% and CEM B 0.7 wt.% K₂SO₄. In both cements the content of potassium sulphate was increased in three steps (Table 2). On that way high alkaline cements are simulated. In practice higher alkali quantities than 1.0 wt.% K₂O_{ws} (1.8 wt.% K₂SO₄) are not found. For the present investigation higher alkali levels were chosen to enhance the effects and to compare the data with findings for regular alkali contents.

Table 2 – Potassium sulphate content of cements in wt.% (in brackets: respective amount of water soluble K₂O)

CEM	K ₂ SO ₄	1	2	3
A	0.6	1.6 (0.9)	2.5 (1.4)	4.5 (2.6)
B	0.7	1.4 (0.9)	1.8 (1.0)	2.6 (1.5)

In both cements the sodium sulphate content of the mixing water was increased to the same molarities as potassium sulphate (i.e. 0.14, 0.28, 0.57 M for CEM A, 0.12, 0.18, 0.29 M for CEM B). Water to cement ratio was 0.4 for mixes of CEM A and 0.39 for CEM B.

2.2 Scanning Electron Microscopy (SEM)

Observation of early cement hydration was carried out with an Environmental SEM (FEI, Netherlands) equipped with a Field Emission Gun (ESEM-FEG). The operational parameters for the “Environmental” mode were the following: water vapour pressure in the chamber was set to 10 – 12.5 mbar and sample temperature to 12 °C. According to this the relative humidity was kept between 75 and 90 % for the area of the cooled sample. Micrographs were taken at 25 keV acceleration voltage. For ESEM observations of the early cement hydration it is crucial to avoid drying artefacts. Three adjustments to address this problem were made: the first step (outside the microscope chamber) was to remove the residual solution with filter paper. Then the sample was immediately inserted into the microscope chamber, where the desired pressure and

temperature were achieved after approx. 3 minutes. The second step of sample preparation was carried out inside the chamber: a few millimetres of the sample surface were removed by scratching with a micromanipulator. A third preparation procedure was carried out on selected samples known to be prone to produce extra hydration products during environmental adjustments in the SEM in the following manner: pastes have been washed several times in ethanol and blotted with filter paper in order to remove the solution of the cement paste and then inserted into the microscope. By having established this set of procedures we compared morphologies of syngenite and detected residues of the pore solution. At the surface of the samples that were not washed with ethanol, residues of the pore solution cover the cement and ettringite grains. Additionally agglomerates of long prismatic crystals (syngenite) occur on the surface. By ethanol washing these structures can be avoided. But no matter how intense the ethanol washing was, some syngenite crystals were always observed. On that way we were able to prove that the detected hydration products resulting from the addition of alkali sulphates (i.e. syngenite) are not drying artefacts.

2.3 X-ray diffraction

Cement pastes were mixed by hand. The hydration was stopped by adding 2-propanol to the paste and subsequent drying at 35 °C. To enhance the syngenite amount for quantification, the silicate clinker phases were removed by selective dissolution in salicylic acid methanol solution. All samples were ground to a grain size below 45 µm. Because only short hydration periods were investigated it has been assumed that the samples contain only a small amount of amorphous phases. Therefore, no internal standard was added. Measurements have been performed with an X-ray powder diffractometer (D-5000, Siemens, Germany).

The CuK α ($\lambda = 1.5418 \text{ \AA}$) radiation was generated at 40 mA and 40 kV. Data have been collected over a Bragg angle range of 8-60° (2 θ), using an angular step width of 0.05° and 5 s counting time. Quantification was done by Rietveld analysis with software Autoquan (BGMN, Germany).

2.4 Viscometric testing

Fluidity of the cement pastes was determined with a speed controlled rotational viscometer (Viskomat NT, Schleibinger, Germany). This measuring system consists of a stationary paddle which is mounted concentrically in a rotating cylindrical vessel. The shear resistance of the sample flowing around the stationary paddle generates a torque which is continuously monitored. Generally in ideal liquids, fluidity is the reciprocal of viscosity. Since cement suspensions possess yield strength and non linear flow behaviour, the fluidity of cement pastes depends on shear rate, yield strength and viscosity. By the applied viscometric measurement it is not possible to discriminate yield strength and viscosity. Therefore in the

following the term fluidity is used to describe the consistency of pastes. The axial torque of the paddle at constant rotational speed (60 rpm) was recorded over time (120 minutes). Measurements were carried out at 20 °C. Cement pastes were prepared according to a defined mixing procedure (6 min low speed mixing in Hobart mixer).

Concrete consistency was tested by slump test (EN 12350-2: 1999). Mix proportions of concrete were as follows: maximum grain size of aggregates 16 mm, 1744 kg aggregates / 405 kg CEM B , w/c of 0.6, one batch of concrete was mixed with addition of 1.2 % K_2SO_4 (referring to the amount of cement) to the mixing water.

2.5 Extraction and analysis of pore solution (cement paste)

Samples were mixed by hand at w/c of 0.4. Extraction of the solution was accomplished by centrifugation for 10 minutes at 15.550 g. Additionally the solution was filtered through a 0.45 μm syringe filter. Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES, Optima 3000, Perkin-Elmer, USA) was used to measure Ca, Na, K, S, Al, Mg, Si and Fe concentrations. The pH-value was measured with a glass electrode.

3 Results

3. 1 Influence of potassium sulphate on fluidity and microstructure of cement pastes

Measurements with the viscometer express fluidity by a value of torque. An increase in torque is equivalent with a decrease in fluidity of the cement paste and vice versa. Figure 1 shows the influence of potassium sulphate content and hydration time on the measured torque (fluidity). Generally with increasing potassium sulphate content the torque is

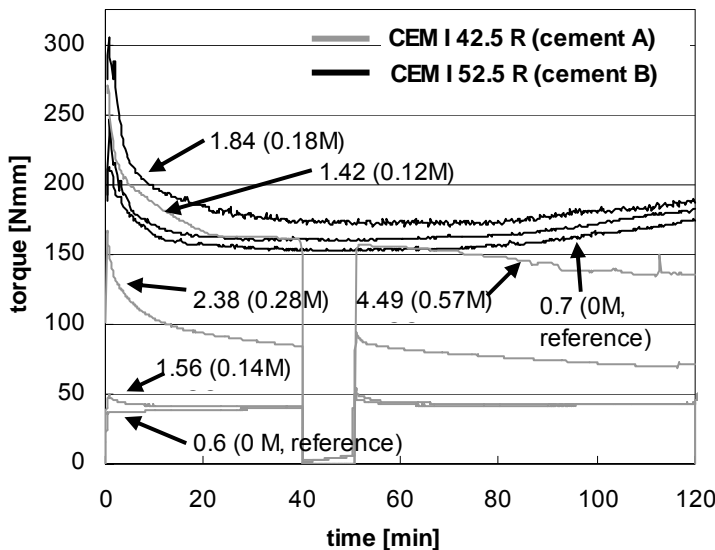


Fig. 1: Results of viscometer measurements: torque in dependence of hydration time and various quantities of potassium sulphate (quantities are given as wt.% referring to the amount of cement, value in bracket denotes molarity M [mol/l] of mixing water).

increased, i.e. the fluidity is decreased. For CEM B the paste with 2.6 % potassium sulphate developed a fluidity that was beyond the detection limits of the viscometer (i.e. > 300 Nmm). Within the first 5 minutes of measurement the torque over time curves for cements with high potassium sulphate concentration show an increased maximum in torque (Fig. 1).

Investigations of the cement paste microstructure (ESEM) on ethanol washed and unwashed samples clearly show that by increasing the

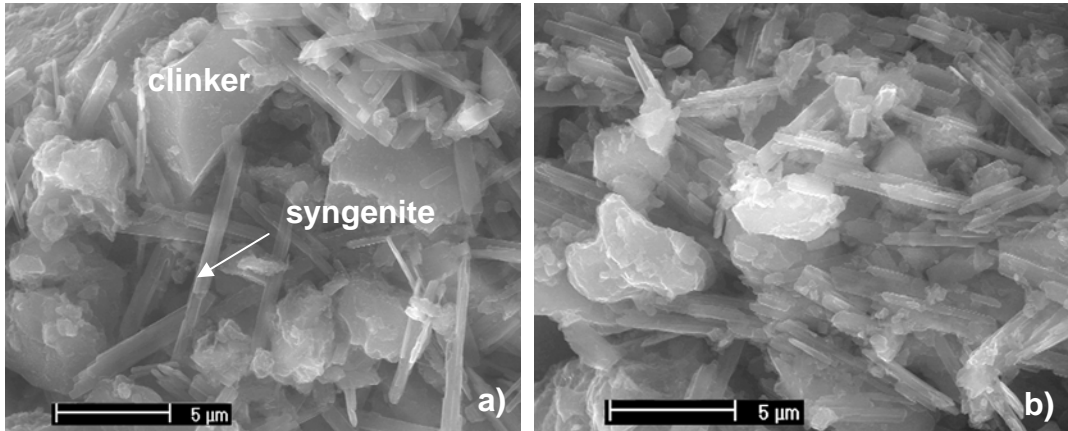


Fig. 2: Syngenite formation imaged by ESEM after 2 hours of hydration of CEM A with 4.49 wt.% potassium sulphate. a) cement hydrated without agitation; random orientation of syngenite crystals b) cement paste after 2 h of shearing in the viscometer; preferred orientation of syngenite crystals.

amount of potassium sulphate an increased quantity of long prismatic crystals is observable. By ESEM these crystals were first detected after a hydration period of ~5 min and stayed part of the microstructure over the investigated 2 hours of hydration. The dimensions of these crystals are approx. 2-10 µm long and 0.2 µm thick (0.5-1 µm wide (Fig. 2a). This typical morphology and results of microanalysis (EDX, results not shown) in the ESEM indicated that those crystals are syngenite. Figure 2b shows that after 2 hours of stirring in the viscometer the typical morphology of syngenite is unchanged but a preferred orientation of crystals (alignment in shear direction) is visible.

Additionally to this qualitative detection of syngenite, results of XRD-Rietveld quantification on CEM B confirmed the findings and are shown in Figure 3. The obtained data clearly show that if the amount of potassium sulphate was increased by factor of 2 the syngenite content of the cement paste was doubled too. Comparison with results of viscometer measurements (Fig. 1) reveal that a syngenite content of 1 wt.% (referred to the amount of cement) results in a significant decrease of the cement paste fluidity.

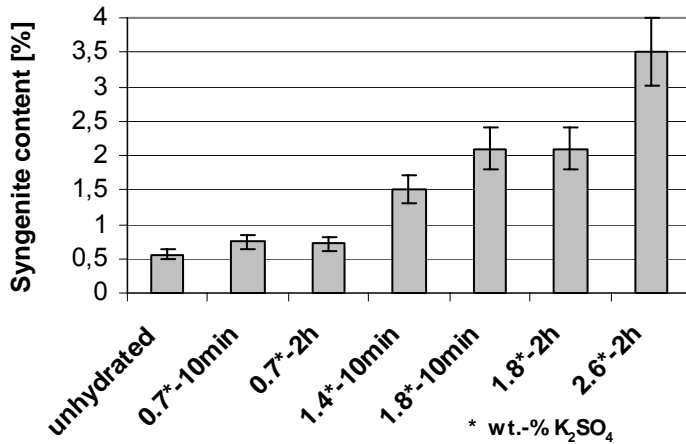


Fig. 3: Syngenite content of CEM B (determined by XRD-Rietveld analysis) in dependence of potassium sulphate content of cement and hydration time.

3.2 Influence of potassium sulphate on concrete fluidity

Results of concrete slump test are shown in Figure 4. Data reveal that an increased potassium sulphate concentration of the cement leads to a reduced concrete slump during the first 30 min of hydration. After 60 and

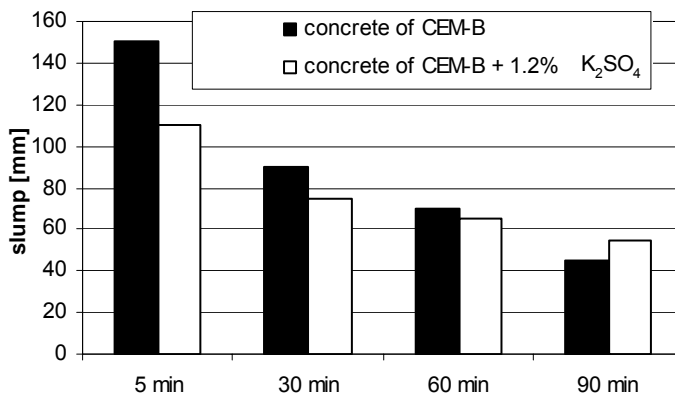


Fig. 4: Time dependent concrete slump (according to EN 12350-2: 1999) for two batches of concrete with increasing potassium sulphate content.

90 minutes of hydration the measured differences are within the detection limit of the measurement.

Comparing with fluidity of cement pastes (CEM B, Fig. 1) it is obvious that potassium sulphate also decreases the fluidity of concrete. During the first 30 minutes of hydration the results show a major decrease in concrete and cement paste fluidity due to increased potassium sulphate content. At later stages of hydration the difference in fluidity, that result from increased potassium sulphate content, decrease for both the concrete and cement paste. Generally slump is correlated with yield stress [25]. The torque measured at the viscometer is influenced by both factors: viscosity and yield stress. For the investigated cement pastes this means that the

loss in fluidity as detected by the viscometer is at least partly caused by increased yield stress.

3.3 Influence of sodium sulphate on fluidity of cement paste

No syngenite or equivalent sodium containing mineral is formed if the sodium sulphate content in the cement paste is increased. Thus, by addition of sodium sulphate the influence of higher ionic strength in the pore solution on the fluidity is evaluated.

The molarities of sodium sulphate in the mixing water were adjusted to the same levels as potassium sulphate. Figure 5 shows the fluidity of cement

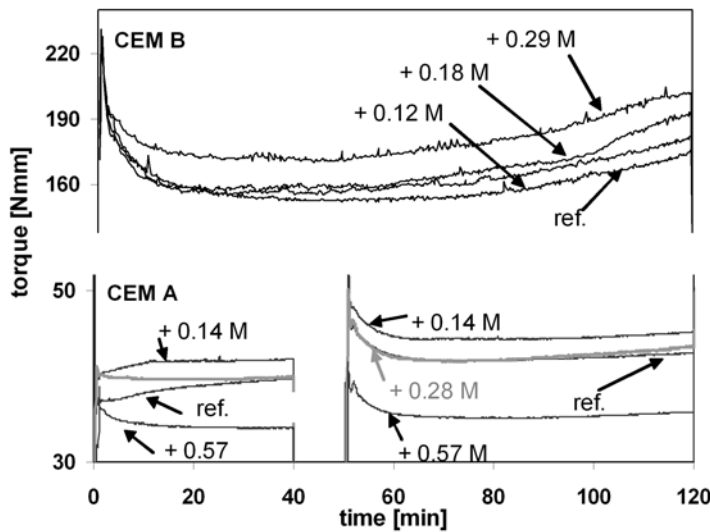


Fig. 5: Influence of sodium sulphate content of the mixing water (indicated for example as “+0.14 M” = mixing water with 0.14 mole per liter [M] Na_2SO_4) on the fluidity (torque) of cement pastes for two different CEM I during the first 2 hours of hydration.

pastes in dependence of sodium sulphate content. Compared to the addition of potassium sulphate the fluidity loss is very minor when low molarities of sodium sulphate were added. At the highest molarity the fluidity of CEM A is even improved. In contrast the fluidity of CEM B is diminished by addition of 0.29 M Na_2SO_4 solution as mixing water. It is important to note that the maximum in torque (minimum in fluidity) within the first 10 minutes is unchanged by addition of sodium sulphate.

4 Discussion and Conclusions

If significant syngenite quantities are formed during cement hydration, a loss in fluidity (maximum in torque) is detected. Because the maximum in torque correlates very well with the time of syngenite formation, it is clearly indicated that crystallisation of this mineral affects the fluidity of the cement paste. This view is supported by the fact, that addition of sodium sulphate to cement paste does not significantly influence the fluidity of the paste. If the mineral quantity that is formed is significant to diminish the fluidity, depends on the starting consistency of the mixture, i.e. water-to-

cement ratio etc. For the investigated CEM B (CEM I 52.5 R), at water-to-cement ratio of 0.39, it was shown that formation of 1 wt.% syngenite results in a marked loss in fluidity. Furthermore it was shown that gain in fluidity is achieved by continuous shear of the paste in the viscometer (at constant rotation speed).

Present models for the rheological behaviour of cement pastes describe the fluidity by means of particle flocculation / coagulation due to interparticle forces (van der Waals and / or electrostatic attraction [7]). The basic assumption is that due to the high ionic strength of the pore solution the particles are always flocculated / coagulated [10]. By increasing the amount of alkali sulphates, the ionic strength (calculated according to [10]) of the cement pore solution is increased. For example addition of 0.28 M K_2SO_4 solution to CEM A increases the ionic strength of the pore solution from 0.22 (reference) to a value of 0.71. The addition of the same molarity sodium sulphate increases the ionic strength to 0.96. According to Flatt et al. [11] higher ionic strength of the pore solution might be a cause for a stronger flocculation and a varied fluidity of the paste. Results of the present study showed that only the addition of potassium sulphate leads to a significant fluidity decrease. But the ionic strength of the pore solution was significantly increased by the addition of both alkali sulphates. Therefore it is concluded that the fluidity decrease does not originate from increased flocculation / coagulation state. But rather, that the crystallisation of syngenite has a marked influence on cement and concrete fluidity.

A further reduction in fluidity that is caused by addition of alkali sulphates might originate from additional gypsum or ettringite formation. Beyond this the pH-value of the cement pore solution is increased by addition of alkali sulphates. According to [3] this can result in a higher hydration degree of clinker phases and diminished cement paste fluidity. Investigations of that sample by ESEM revealed no additional hydration products like gypsum. Results of XRD-Rietveld analysis (data not shown) showed that C_3A consumption was not significantly altered (i.e. variations <1 wt.%). Thus it is further indicated that in the presence of relevant potassium sulphate contents the fluidity is influenced solely by crystallisation of syngenite.

According to the flocculation model the floc structure is destroyed by mixing and rebuilt at rest of the paste. In order to evaluate the contribution of increased flocculation / coagulation on the fluidity the measurements of CEM A were halted after 40 min and restarted after 50 min (Figs. 1 & 5). The magnitude of the torque maximum after restart is approx. ≤ 10 Nmm for all investigated cement pastes. It is always lower than the maxima caused by syngenite formation within the first 10 minutes of hydration (Fig. 1). From that we deduce that compared to formation of long prismatic / elongated crystals, the increased ionic strength and the following

flocculation / coagulation has a minor impact on cement paste fluidity. Furthermore it is deduced that after 40 minutes of hydration, the precipitation rate of syngenite is marginal as compared to the very first minutes of hydration.

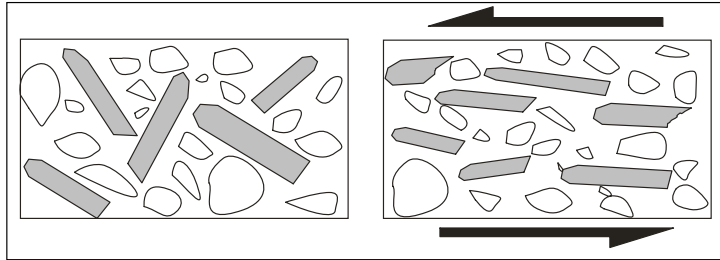


Fig. 6: Rotation of syngenite crystals into the shear direction (indicated by arrows), development of a preferred orientation.

General rheological models for suspension indicate that two competing processes induce the minimum and subsequent gain in fluidity: a) an increasing formation of hydrate phases [20] and b) the movement of particles (for example hydrate phases) in the sheared suspension [22-24]. For process a) it is known that with increasing asymmetry of particles (from spheroid to rod like) the viscosity of a suspension increases [25]. For b) according to the rheological models it is expected that elongated particles rotate into the shear direction [22, 27]. The formation of a preferred orientation of elongated particles in the shear flow results in fluidity gain. Figure 6 illustrates the process of alignment of syngenite in simple shear conditions of cement paste. If the syngenite crystallisation rate is high and the orientation of the new formed crystals is random to the shear (flow) direction the fluidity of the cement paste is lowered. Continuous shear leads to rotation of syngenite crystals. Thereby a preferred orientation is developed. This process is accompanied by an increase in fluidity (decrease in viscosity and yield stress).

Viscometer measurements at constant rotational speed are affected by both factors that define fluidity: apparent viscosity and yield stress. It is known that the crystallisation of elongated crystals affects not only the viscosity but also the yield stress of suspensions [24, 25]. Kurdowski and Grzeszczyk [18] showed that yield stress and plastic viscosity of cement pastes increases when potassium sulphate concentrations exceed a certain value. Since slump is regarded to correlate with yield stress we confirmed the findings of [18]. Additionally it was shown that the concrete yield stress is increased by potassium sulphate concentration and that the formation of 1 wt.% syngenite has a marked influence on fluidity of the investigated cement paste.

5 References

- [1] J. Gebauer, Technological possibilities of avoiding the early setting of cement, *Zement-Kalk-Gips* 31 (1978) 302-304
- [2] J. Bensted An Investigation of the setting of Portland cement, *Silic Ind* 45 (1980) 115-120
- [3] E.M. Gartner, J.F. Young, D.A. Damidot, I. Jawed, Hydration of Portland cement in: J. Bensted, P. Barnes (Eds.) *Structure and performance of cements*, Second edition Spon Press, London and New York. 2000, 57-113
- [4] J. P. Skalny, J.F. Young, Mechanisms of Portland cement hydration, in: *Proc. 7th ICCG, Paris Vol. I, part II, 1980, II 1/3-1/45*
- [5] J. Stark, B. Möser, F. Bellmann, New approaches to cement hydration in the early hardening stage, in: *Proc. 11th ICCG, Durban, Techbook International, New Delhi, India, 2003, 261–278*
- [6] A. Nonat, J. C. Mutin, From hydration to setting, in: A. Nonat, J. C. Mutin (Eds.), *Hydration and Setting of cements, Proc of the Intern RILEM Workshop on Hydration and Setting, E&FN SPON, London, 1992, 171-191*
- [7] T. C. Powers, *The Properties of fresh concrete*, New York, NY [u.a.] : Wiley, 1968
- [8] P.M. McGuiggan, J.N. Israelachvili, Short-range and adhesion forces between surfaces in aqueous electrolyte solutions: interplay of DLVO and hydration forces, in: A. Nonat, J. C. Mutin (Eds.), *Hydration and Setting of cements, Proc of the Intern RILEM workshop on Hydration and Setting, E&FN SPON, London, 1992, 205-217*
- [9] H. Haidara, Fundamental mechanisms of adhesion: relevance to particle interactions, sticking and aggregation in a fluid medium, in: A. Nonat (Ed.) *Hydration and Setting – Why does cement set? An interdisciplinary approach. Proc of the second Intern RILEM workshop, RILEM Publications S.A.R.L. Cachan Cedex, 1997, 3-22.*
- [10] M. Yang, C.M. Neubauer, H.M. Jennings, Interparticle potential and sedimentation behaviour of cement suspension - Review and results from paste, *Advn Cem Bas Mat*, 5 (1997) 1-7
- [11] R.J. Flatt, Dispersion forces in cement suspensions, *Cem and Concr Res* 34 (2004) 399-408
- [12] A. Kauppi, P.F.G. Banfill, P. Bowen, L. Galmiche, Y.F. Houst, F. Lafuma, U. Mäder, F. Perche, B.G. Petersen, K. Reknes, I. Schober, A. Siebold, D. Swift, Improved superplasticizers for high performance concrete, in: *Proc. 11th ICCG, Durban, Techbook International, New Delhi, India, 2003, 528–537*
- [13] R.J. Flatt, Towards a prediction of superplasticized concrete rheology, *Mat and Struct.* 37 (2004) 289-300
- [14] J.P. Bombled, Influence des sulfates sur les comportements rhéologiques des pâtes des ciment et sur leur evolution, in: *Proc. 7th ICCG, Paris Vol. III, 1980, pp 164-169*

- [15] H. Uchikawa, K. Ogawa, S. Uchida, Influence of character of clinker on the early hydration process and rheological property of cement paste, *Cem and Concr Res*, 15 (1985) 561-572
- [16] F. J. Tang, E.M. Gartner, Influence of sulphate source on Portland cement hydration, *Adv Cem Res*, 1 (1988) 67-74
- [17] S. Grzeszczyk, The influence of the early stage of hydration of cement paste on their consistency and strength, in: A. Nonat, J. C. Mutin (Eds.), *Hydration and Setting of cements*, Proc of the Intern RILEM workshop on Hydration and Setting, E&FN SPON, London 1992, 315-322.
- [18] W. Kurdowski, S. Grzeszczyk, The influence of K_2SO_4 on action of superplasticizers and properties of cement paste and mortar, in: A. Nonat (Ed.) *Hydration and Setting – Why does cement set? An interdisciplinary approach*. Proc of the second international RILEM workshop, RILEM Publications S.A.R.L. Cachan Cedex, 1997, 403-417
- [19] W. vom Berg, Influence of specific surface and concentration of solids upon the flow behaviour of cement pastes, *Mag Concr Res*, 31 (1979) 211-216
- [20] P. F. G. Banfill, Simultaneous measurements of hydration rate and rheology on cement pastes, in: A. Nonat, J. C. Mutin (Eds.), *Hydration and Setting of cements*, Proc of the Intern RILEM workshop on Hydration and Setting, E&FN SPON, London, 1992, 267-278
- [21] A. W. Saak, H. M. Jennings, S. P. Shah, A generalized approach for the determination of yield stress by slump and slump flow, *Cem Concr Res* 34 (3) (2004) 363-371
- [22] G.B. Jefferey, The motion of ellipsoidal particles immersed in a viscous fluid, *Proc. R. Soc. London Ser. A* 102 (1922) 161–179
- [23] H. L. Goldsmith, S. G. Mason, *Microrheology of dispersions*, in: F.R. Eirich (Ed.), *Rheology*, Vol.4, Pergamon, New York, 1967, 85-250.
- [24] S. K. Gosh, H. Ramberg, Reorientation of inclusions by combination of pure and simple-shear, *Tectonophys* 34 (1976) 1-70
- [25] H. Brenner, Rheology of a dilute suspension of axisymmetric Brownian particles, *Intern J Multiphase Flow* 1 (2) (1974) 195-341