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Influence of hydration on the fluidity of normal Portland cement pastes

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ABSTRACT

The rheological properties of cement paste strongly influence the workability of concrete. It is known that early hydration processes alter phase composition and microstructure of cement pastes. These processes affect fluidity and setting behaviour of cement paste. While many studies tried to measure and model rheological properties of cement pastes, only a few studies assessed the influence of the hydrate morphology on the fluidity of cement pastes.

Results of the present study compare the influence of long prismatic hydrates (i.e. syngenite, secondary gypsum) on the fluidity of cement pastes with the effect of other hydrates (AFm).

To induce the formation of certain hydration products the cement composition was modified by addition of set regulators and alkali sulphates. Furthermore a combination of various analytical methods such as fluidity (viscometric) testing and microstructural analysis (phase quantification by XRD-Rietveld analysis, investigation by Environmental SEM, BET analysis etc.) was performed. Results are implemented into a fundamental discussion on the influence of various hydration products on the fluidity of the paste.

1. Introduction

Predictable workability is of great importance in the design of modern concretes (self levelling concretes as well as high and ultra high performance concretes). Production of those concretes depend on the availability of concrete admixtures like modern superplasticizers. Ideally superplasticizers should be applied to induce targeted concrete flow characteristics. Thus many investigations have been carried out to reveal the mode of action of superplasticizers in cement and concrete [1–3]. The basic assumption on most of the studies is that the fluidity of cement paste influences the workability of concrete. Thereby the fundamental processes that determine fluidity and setting of cement paste are still being discussed. Known key parameters that control the fluidity of cement pastes are: particle size distribution, volume fraction of particles respective aqueous phase, interparticle forces and hydration progress.

Before setting (ASTM C191/DIN EN 196-3), concrete has to be placed. The reason is that with progressing hydration time cement paste—and thus concrete—encounter physical and chemical processes that reduce the fluidity significantly. In the period before setting the fluid properties of cement pastes dominate. Setting of cement paste is defined by Vicat-needle test according ASTM C191/DIN EN 196-3. It is generally accepted that at setting time cement pastes plastic (fluid-like) deformation behaviour is lost to a certain extend. 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 [4–7].

Various testing methods are applied to document changes in cement paste fluidity [8,9]. Powers [10] considered that the rheological behaviour of normal Portland cement pastes is caused by several forces: van der Waals forces, electrostatic forces and or hydration forces. According to Powers [10] and following studies [11–13] these forces cause the agglomeration/flocculation of cement particles. Recently Flatt et al. [14] and Kauppi et al. [15] tried to model and to measure these forces. The aim is to predict plastic viscosity and yield stress of cement paste [11,16].

Other investigations [17–22] showed the dependence of fluidity on cement characteristics for example: specific surface area of cement (particle size distribution), clinker and set regulator composition etc.

Several authors [18,23] suggested that formation of ettringite increases the interparticle interaction and this leads to an increased viscosity of the cement paste.

In the presented study we qualitatively and quantitatively characterized cement hydration, microstructure and changes in specific surface area of cement. Fluidity of cement paste in dependence of hydration period and cement composition was determined by viscometric testing. By combining results of the various techniques it is possible to improve the basic understanding on how the formation of hydration products influences the cement paste fluidity. Thus we have been able to evaluate the influence of hydration products like syngenite and AFm phases on the fluidity of cement pastes. Exemplary studies on concrete fluidity

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

Cement	CaO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	K_2O_{ws}	Na_2O_{ws}	SO_3	CaO_f	MgO
A	63.2	20.3	6.0	3.1	0.55	0.11	0.32	0.04	2.8	0.7	1.1
B	66.0	22.9	4.0	1.3	0.66	0.23	0.40	0.06	3.1	<0.09	0.6

have been carried out to determine if an increased quantity of syngenite crystals in cement paste influences concrete fluidity.

2. Materials and methods

2.1. Cements

Two commercial cements of type CEM I 42.5 R (cement A) and CEM I 52.5 R (cement B) according to European Standard DIN EN 197-1 as well as several laboratory made cements were used.

Chemical composition of studied cements is given in Table 1. Both are low alkali cements.

XRD-Rietveld analysis was applied to quantify the mineral phase composition of cements (Table 2). For cement B contents of C_3A and C_4AF have been determined on residues of salicylic acid methanol extraction. Comparing the mineral composition of cements A and B it becomes obvious that C_3A content is equal but set regulator composition varies. The most significant mineralogical difference that might influence fluidity of both cements is therefore, that cement B contains highly soluble bassanite as set regulator. Another marked difference is the specific surface area of the cements, which is for cement A 300 m^2/kg (Blaine) and for cement B 500 m^2/kg (Blaine).

The first batch of laboratory cements were composed by addition of defined set regulators (calcium sulphates) to clinker of cement A (specific surface area: 300 m^2/kg Blaine). Added set regulators possess different dissolution properties. The following five different set regulators were used for investigations (in wt.% of cement):

1) 4 anhydrite (4 ah),
2) 1 anhydrite and 2 bassanite (1 ah–2 bas),
3) 1 anhydrite and 3 bassanite (1 ah–3 bas),
4) 4 gypsum (4 gy),
5) 4 bassanite (4 bas).

P.a. substances of bassanite ($CaSO_4 \cdot 0.5\ H_2O$, Baker) and gypsum ($CaSO_4 \cdot 2\ H_2O$, Merck) and anhydrite ($CaSO_4$, Merck) with a specific surface of 690, 600 and 700 (Blaine) respectively were used for investigations. Prepared laboratory cements were homogenized for 1 h in an asymmetric moved mixer.

In a second batch of laboratory cements potassium sulphate was added to the mixing water in order to increase the amount of soluble alkalis in the commercial cements. By assuming that all water soluble potassium is bound to sulphate commercial cement A contains 0.6 wt.% and commercial cement B 0.7 wt.% K_2SO_4. In both cements the content of potassium sulphate was increased in three steps (Table 3). On that way high alkali cements are simulated. The benefit of alkali sulphate addition to the mixing water (instead of using high alkali cement) is that the reactivity of aluminate—due to incorporation of alkali ions—is unchanged.

In practice higher alkali quantities than 1.0 wt.% K_2O_{ws} (1.8 wt.% K_2SO_4) 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.

In a third batch 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 cement A, 0.12, 0.18, 0.29 M for cement B. On this way all batches of cements A and B were supplied with sodium respectively potassium sulphate at the same ionic strength of the mixing water.

Water to cement ratio was 0.4 for mixes of cement A and 0.39 for cement B.

2.2. Scanning electron microscopy (SEM)

Microstructure of cement pastes was imaged 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 10.5–12.5 mbar and sample temperature to 12 °C. According to pressure and temperature, 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 aqueous 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 min. 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 aqueous phase 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 aqueous phase of cement paste. At the surface of the samples that were not washed with ethanol, residues of the aqueous phase cover the cement and ettringite particles. Additionally agglomerates long prismatic crystals (syngenite) occur. These structures can be avoided by ethanol washing. No matter how intense the ethanol washing was, the typical syngenite crystals below the surface 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.

In order to enhance the syngenite amount for quantification, the silicate clinker phases were removed in cement B by selective dissolution in salicylic acid methanol solution. Because of the high iron content of cement A, and resulting high anomalous dispersion of CuKα X-rays [24], this procedure was not applied for cement A.

Table 2
Mineral phase composition of cements determined by XRD-Rietveld (wt.%)

Cement	$C_3S \pm 3.0$	$C_2S \pm 2.0$	$C_3A \pm 1.0$	$C_4AF \pm 1.0$	Gypsum ± 0.3	Bassanite ± 0.4	Anhydrite ± 0.2	Syngenite ± 0.07	Calcite ± 1.0
A	52	21	8	10	1.9	–	2.6	–	4.0
B	62	16	8	4	0.9	2.3	1.7	0.56	3.4

Table 3
Potassium sulphate content of cements in wt.% (in brackets: respective molarity, M = mol/l, of mixing water due to K_2SO_4 addition)

Cement	Reference	1	2	3
A	0.6 (0)	1.6 (0.14)	2.5 (0.28)	4.5 (0.57)
B	0.7 (0)	1.4 (0.12)	1.8 (0.18)	2.6 (0.29)

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 CuKα ($\lambda = 1.5418$ Å) radiation was generated at 40 mA and 40 kV. Data have been collected over a Bragg angle range of 8–60° (2θ), 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. Fluidity 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 sample flowing around the stationary paddle generates a torque which is continuously monitored. The axial torque of the paddle at constant rotational speed was recorded over time.

Measurements were carried out at 20 °C. Cement pastes were prepared as follows: 1. Cement was added to water in a Hobart mixer (1.5 min mixing, 0.5 min pause, 4 min mixing), 2. After 6 min the measurement was started, 3. Torque was measured for 120 min at constant rotation speed (60 rpm) of the vessel.

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 cement 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. Testing was carried out immediately after mixing (7 min of hydration) as well as after 30, 60 and 90 min hydration.

2.5. Determination of specific surface area by N_2 BET analysis

The specific surface area (SSA) of hydrated and unhydrated cement was determined by measuring isothermal N_2 adsorption isotherms with the SA 3100 S (Coulter, USA). Hydration was stopped as described for XRD analysis. For measurement of N_2 adsorption isotherms the adsorbed water has to be removed from the sample. Therefore the apparatus evacuates sample with a pressure of $1.04\ \ 10^{-2}$ mbar at a temperature of 40 °C.

For the applied preparation procedure maximum deviation from the given mean value is 0.05–0.08 m^2/g.

2.6. Extraction and analysis of aqueous phase of cement paste

Samples were mixed by hand at w/c of 0.4. Extraction of the solution was accomplished by centrifugation for 10 min 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 alkali sulphates on fluidity and microstructure of cement pastes

3.1.1. Influence of potassium sulphate on fluidity and microstructure of cement pastes

Viscometer measurements 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.

Fig. 1 shows the measured torque (fluidity) over hydration time in dependence of potassium sulphate content. By comparing fluidity of cements A and B reference pastes it becomes obvious, that at similar w/c the fluidity of cement A is significantly lower. Furthermore only for cement B the typical torque over time curve with the progression of first torque maximum following minimum and subsequent torque slope is detected. The reason that this curve progression is not clearly shown by cement A can be explained as follows: chemical analysis of both cements reveals that both cements are low alkali cements. Thus a variation in C_3A reactivity is not expected. This assumption is validated by the determined $C_3A_{cubic}/C_3A_{orthorhombic}$, which are 1.7 for cement A and 1.3 for cement B. For high alkali cements this ratio decreases to values of for example 0.1. Furthermore it is known that C_3A reactivity decreases with increasing amount of orthorhombic C_3A [6]. Thus cement B should possess a lower C_3A reactivity and consequently fluidity than cement A. This is contrary to the results shown in Fig. 1. Therefore it is assumed that the main cause of the different torque over time curve characteristics is the increased

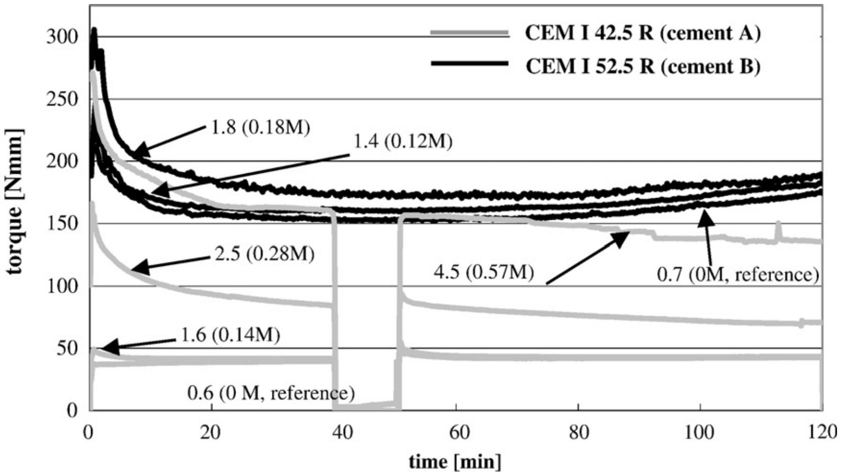


Fig. 1. Fluidity of cement pastes expressed as viscometer torque in dependence of hydration time and potassium sulphate addition (potassium sulphate quantities are given as wt.% referred to the amount of cement, value in bracket denotes molarity M = mol/l, of mixing water).

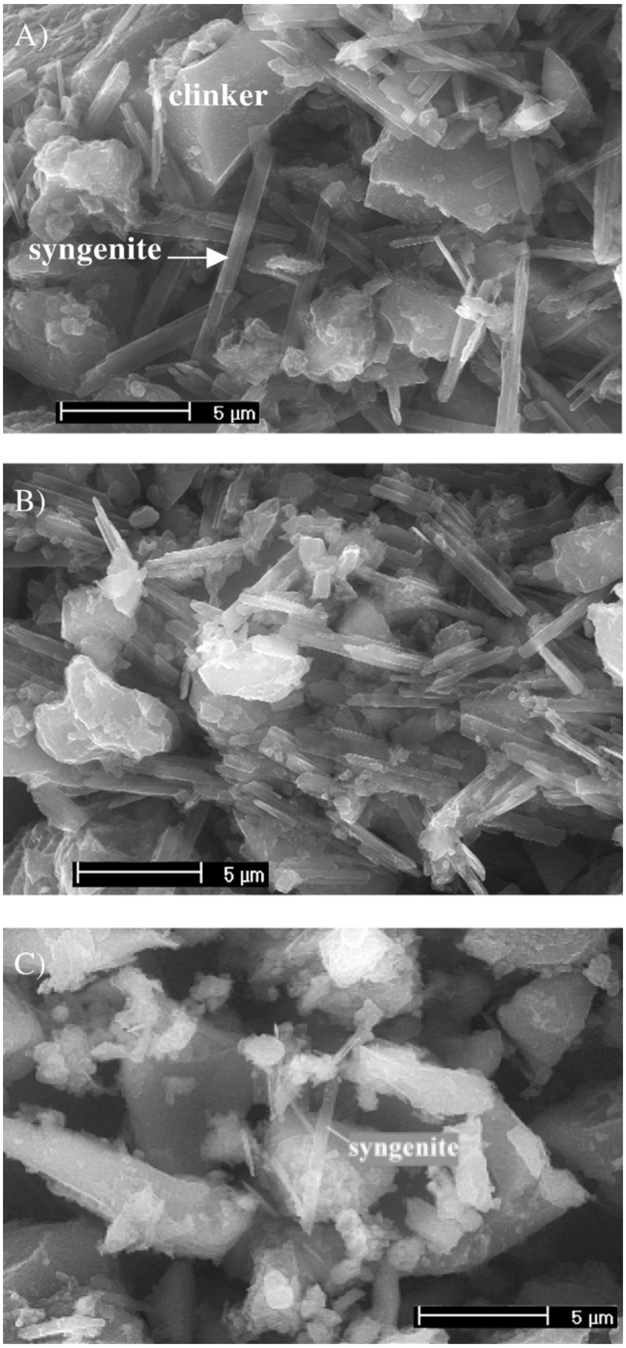


Fig. 2. A, B: Syngenite formation imaged by ESEM-FEG after 2 h of hydration of cement A with 4.49 wt.% potassium sulphate. A) Cement hydrated without agitation; random orientation of syngenite, B) cement paste after 2 h of shearing in the viscometer; preferred orientation of syngenite crystals. C: Cement paste A with 1.56% K_2SO_4 content: minor amount of syngenite (ESEM-FEG, 10 min hydration).

specific surface area of cement B. This results in lower fluidity due to higher water adsorption (due to increased specific surface area) and absorption (due to hydration). Increased water absorption is expected because at increased specific surface area of cements the quantity of clinker (C_3A) that is accessible to react with the mixing water increases. Other factors that might influence fluidity of cement pastes are set regulator composition, free lime content and alkali sulphates.

Furthermore results in Fig. 1 show, that with increasing potassium sulphate content the torque is increased, i.e. the fluidity is decreased. For cement B the paste with 2.6% potassium sulphate developed a fluidity that was beyond the detection limits of the viscometer (i.e. >300 N mm).

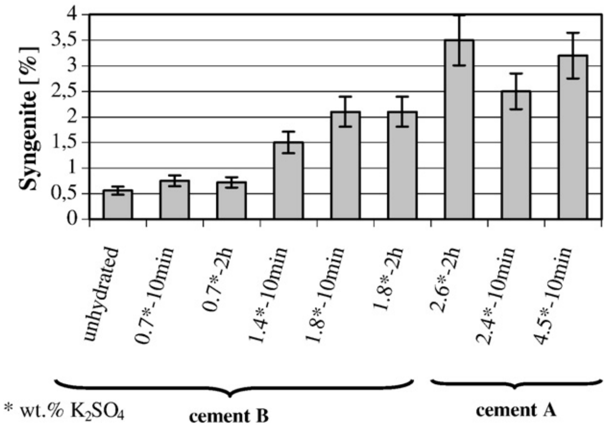


Fig. 3. Syngenite content (determined by XRD-Rietveld analysis) of cements in dependence of potassium sulphate content and hydration time of cement. For cement A containing 1.6% K_2SO_4, syngenite content was beyond detection limit (see text for discussion).

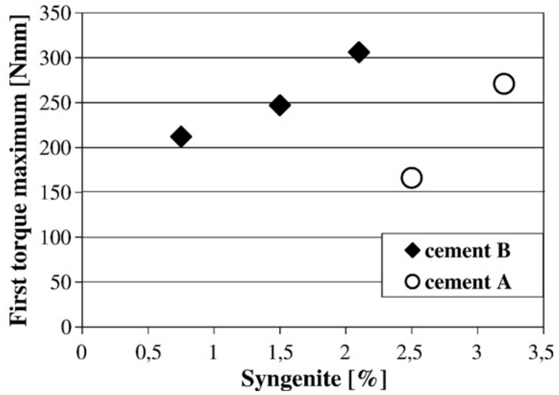


Fig. 4. First maximum in torque (Viskomat NT) of cement pastes in dependence of syngenite content (results of XRD-Rietveld analysis after 10 min of hydration).

Within the first 5 min of the torque over time curves, cements with high potassium sulphate concentration show a maximum in torque (Fig. 1). From Fig. 1 it is obvious that by increasing the potassium sulphate content a significant increase of the torque maximum is detected.

ESEM investigations of the cement paste microstructure were carried out on ethanol washed and unwashed samples of both cements. Observations clearly show that by increasing the amount of potassium sulphate an increased quantity of long prismatic crystals is formed. These crystals were detected immediately after addition of mixing water (~5 min) as well as at all further stages that were

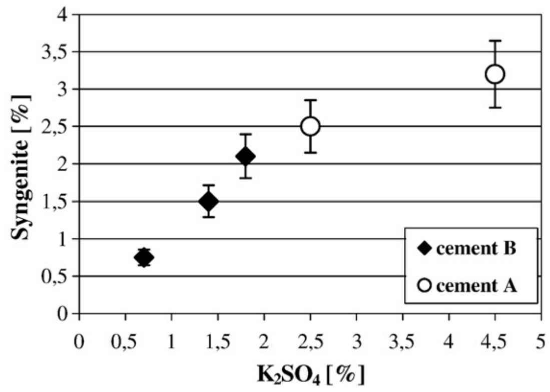


Fig. 5. Syngenite content of cement after 10 min of hydration in dependence of potassium sulphate content.

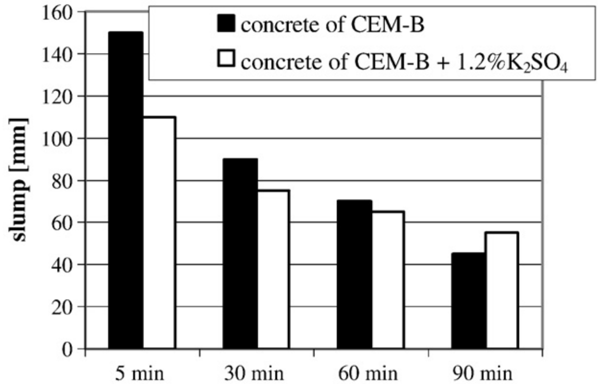


Fig. 6. Time dependent concrete slump (according to EN 12350-2: 1999) for two batches of concrete with increasing potassium sulphate content.

investigated (up to 2 h of hydration). The dimensions of these crystals are: 2–10 μm long and 0.2 μm thick (0.5–1 μm wide, Fig. 2A). This typical morphology and results of microanalysis (EDX) in the ESEM proof that those crystals are syngenite.

Fig. 2B shows that after 2 h of stirring in the viscometer the typical long prismatic habitus of syngenite is still present. Additionally a preferred orientation of syngenite crystals (alignment in shear direction) is visible.

Furthermore to this qualitative detection of syngenite, results of XRD-Rietveld quantification (Fig. 3) confirmed the ESEM findings. Results of XRD-Rietveld analysis in Fig. 3 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. Also it is shown that in cement B syngenite quantities of 0.6 wt.% were detectable. In contrast, for cement A the syngenite detection limit was found to be approximately 2.5%. The reason is that for XRD detection of low syngenite quantities it is essentially to analyse residues of salicylic acid methanol extractions (thereby syngenite content is enriched due to removal of silicate phases). But this approach is not advisable for cement A with high iron content and application of CuKα X-ray radiation [24]. Thus it is assumed that for cement A containing 1.6 wt.% K$_2$SO$_4$ the lacking proof of syngenite by XRD may be due to the low syngenite concentration. Nevertheless ESEM-FEG investigations on this cement paste clearly showed that syngenite is present (Fig. 2C).

Also at the highest amount of added potassium sulphate in cement A the syngenite quantity seems to be fairly low. The reason is that in dependence of pH as well as calcium ion concentrations in the aqueous phase of cement pastes the concentration of potassium and sulphate ions that are enriched may greatly vary. This always results in lower syngenite quantities than expected and also in varying syngenite quantities even if the supply of potassium and sodium ions was similar.

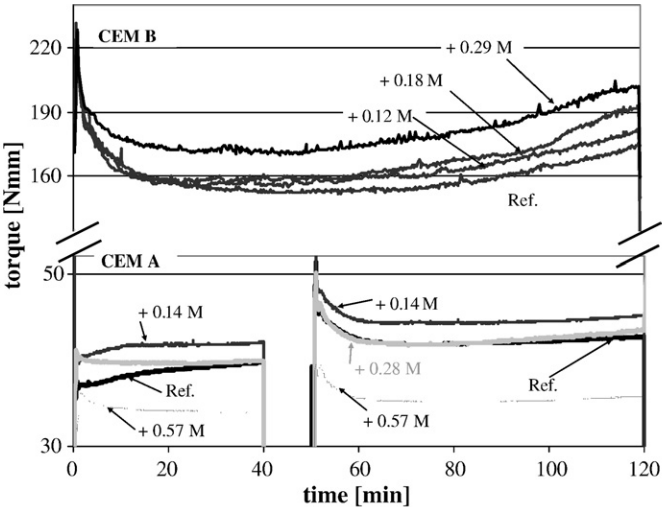


Fig. 7. Influence of sodium sulphate content of the mixing water (indicated as "+0.14 M" = 0.14 M Na$_2$SO$_4$ solution) on the fluidity (torque) of cement pastes for two different cements (CEM I) during the first 2 h of hydration.

Table 4
Ionic strength of aqueous phase of cement pastes

Cement	Ionic strength [M = mol/l]				
	Reference	0.18 M		0.28 M	
		K$_2$SO$_4$	Na$_2$SO$_4$	K$_2$SO$_4$	Na$_2$SO$_4$
A	0.22	–	–	0.71	0.96
B	0.33	0.63	0.79	–	–

Comparison of syngenite contents of cement pastes with viscometer measurements (Figs. 1 and 3) reveals that for cement B a syngenite content of 1 wt.% (referred to the amount of cement) results in a significant decrease of the cement paste fluidity. For cement A this quantity is at least 2 wt.%, because the fluidity of the reference paste is very high. Correlation of syngenite content and first maximum in torque is shown in Fig. 4. Obviously the first torque maximum increases (i.e. fluidity decreases) if syngenite content is increased. Fig. 5 displays that by increasing the amount of potassium sulphate the syngenite content of cement (after 10 min of hydration) increases too. This increase in torque (decrease in fluidity) due to increased syngenite formation is observed over the total period of fluidity testing.

3.1.2. Influence of potassium sulphate content on concrete fluidity

Concrete slump in dependence of hydration time and potassium sulphate addition are shown in Fig. 6. 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 90 min of hydration the measured differences are within the detection limit of the measurement.

Obviously, the slump loss of the reference concrete is higher than that with the potassium sulphate addition. This effect is due to the significantly reduced slump of concrete with increased potassium sulphate content at the beginning (7 min).

Compared to fluidity measurements of the corresponding cement pastes (cement B, Fig. 1), potassium sulphate has a similar influence on the concrete fluidity. During the first 30 min of hydration the investigation reveals a major decrease in concrete and cement paste fluidity due to increased potassium sulphate content. At later stages

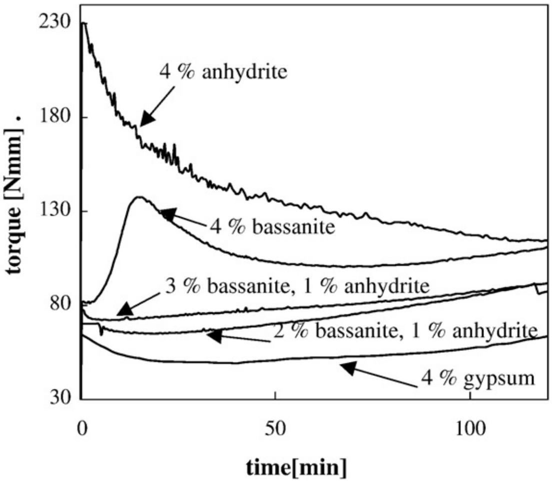
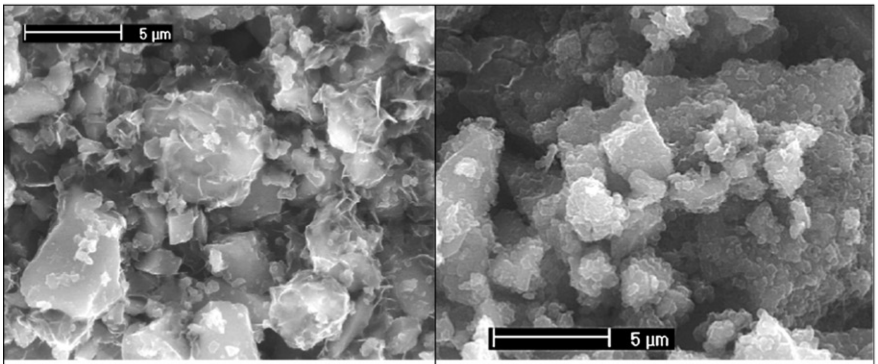


Fig. 8. Fluidity (torque) of laboratory cement pastes (clinker of cement A) in dependence of set regulator compositions (dissolution rates) and hydration period.

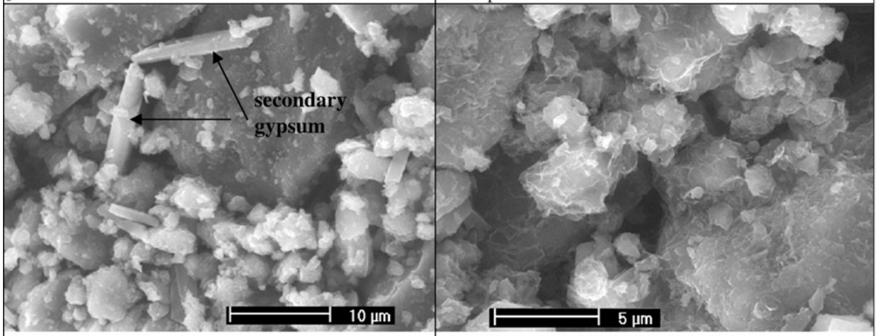
of hydration the difference in fluidity, that result from increased potassium sulphate content, decreases for both the concrete and cement paste.

Generally slump is correlated with yield stress [25]. For the investigated concrete this means that the loss in fluidity as detected by the viscometer is at least partly caused by diminished yield stress.



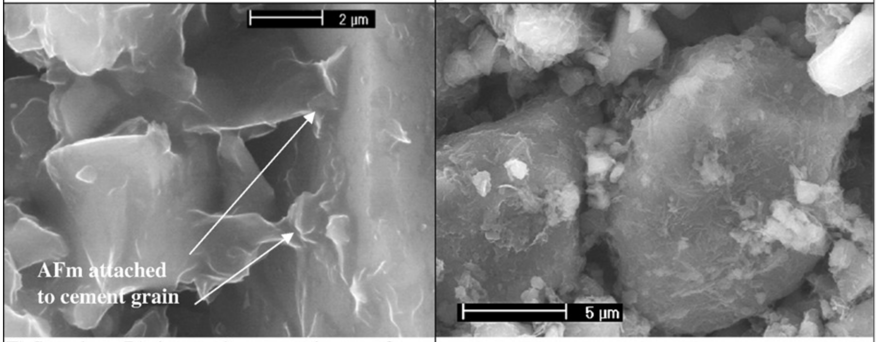
A) Ground clinker 10 min hydrated without set regulator: AFm phases envelope cement particles.

B) Commercial cement (A) 10 min hydrated, ettringite covers cement particles, absence of AFm phases.



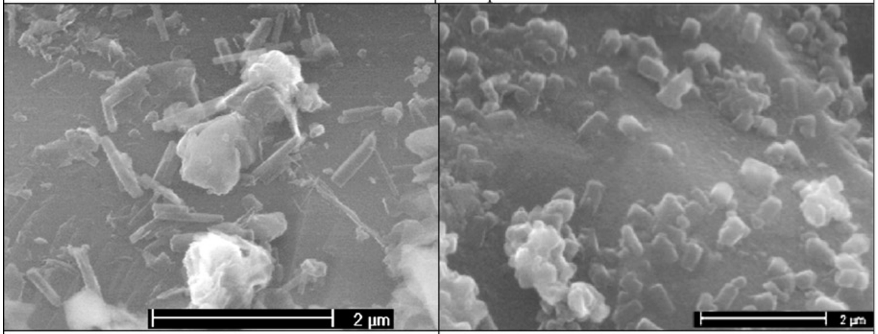
C) Clinker and 4 % bassanite, 1 h hydrated: long prismatic gypsum crystals.

D) Clinker and 4 % anhydrite, 10 min hydrated: AFm phases envelope cement particles.



E) Sample as D), image shows attachment of AFm phases on cement particle.

F) Sample as in figs. D, E) but after 2 hours hydration and shearing: ettringite replaces AFm phases



G) Enlarged image of F) showing long prismatic ettringite on a clinker particle.

H) Cement paste with 3 % bassanite 1% anhydrite; short prismatic ettringite on clinker surface.

Fig. 9. A–G) ESEM-images of cement pastes.

Table 5
Hydration products, Ca and S concentrations in cement pastes in dependence of set regulator composition

Set regulator [wt.%]	Hydration products	Ion concentration [mmol/l]	
		Ca	S
4 bassanite	Short prismatic ettringite, secondary gypsum	57	162
3 bassanite, 1 anhydrite	Short prismatic ettringite, secondary gypsum	52	142
2 bassanite, 1 anhydrite	Short prismatic ettringite, secondary gypsum	27	95
4 gypsum	Short prismatic ettringite	29	83
4 anhydrite	AFm, long prismatic ettringite	18	52
–	AFm	7	2

3.1.3. Influence of sodium sulphate on fluidity of cement paste

It is generally known that 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 sulphate concentration (ionic strength) on the fluidity is evaluated, without modifying the syngenite content.

The molarities of sodium sulphate in the mixing water were adjusted to the same levels as potassium sulphate (Table 3).

According to [26] due to the high pH of the cement pastes it is not expected that the increase in sodium sulphate content induces the formation of secondary gypsum. Microstructural investigations by ESEM-FEG and XRD confirm this assumption (results not shown). Thus it is excluded that the fluidity of cement pastes is influenced by formation of secondary gypsum.

After 10 min of hydration the addition of 0.28 M Na_2SO_4 solution to cement A and 0.18 M Na_2SO_4 solution to cement B increases the pH of the cement paste from 12.9 to 13.09 and 13.03 to 13.12 respectively. This could result in an accelerated C_3A hydration and thus a diminished fluidity. Results of viscometric measurements in dependence of sodium sulphate addition are shown in Fig. 7. Compared to the addition of potassium sulphate the fluidity loss is very minor when low molarities of sodium sulphate were added. The fluidity of cement A is even improved when the mixing water possessed the highest molarity of sodium sulphate. In contrast the fluidity of cement B is significantly 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 min does not vary in dependence of sodium sulphate content.

From these results it is concluded that compared to the influence of potassium sulphate the increase in sodium sulphate content has a very minor influence on cement paste fluidity. Also it was shown that the increased pH value (due to addition of relevant sodium sulphate quantities) does not significantly diminish the cement paste fluidity. In accordance with these findings quantification of C_3A content in cement pastes after 10 min of hydration (XRD-Rietveld) revealed that with increasing alkali sulphate content a significant variation in C_3A content was not detectable; determined C_3A content was approximately 6–7 wt.% for all samples. Thus differences were within the standard deviation of the analysis, ~±1 wt.%.

For exemplary pastes the ionic strength of aqueous phase in dependence of alkali sulphate addition was calculated according to [13] from measured ion concentrations. Results are shown in Table 4. As expected, by addition of alkali sulphates the ionic strength of aqueous phase of cement pastes increases. When potassium sulphate is added, the ionic strength is always lower as compared to sodium sulphate addition. The reason is that potassium and sulphate ions are consumed by syngenite precipitation.

Comparison with measured fluidity reveals that a correlation between fluidity and ionic strength is not obvious.

3.2. Influence of set regulator on cement paste fluidity

Fig. 8 shows results of viscometer measurements (torque) of cement pastes (cement A) in dependence of hydration time and set regulator (calcium sulphate) composition. The added set regulators possess different dissolution rates; anhydrite dissolves slowly, whereas bassanite provides higher concentration of calcium and sulphate ions into the aqueous phase of cement paste after short times.

It is obvious (Fig. 8) that by increasing the dissolution rate of set regulator an optimum fluidity can be achieved (lowest torque values for curve “4% gypsum”). The set regulator composition for optimal fluidity depends on the dissolution rate of the various calcium sulphate minerals. An optimum fluidity over the time was detected for addition of 4% gypsum as set regulator. A diminished fluidity was detected for both low and high dissolution rates of set regulator.

Microstructural investigations of the cement paste after 10 min of hydration by ESEM clearly show that with increasing dissolution rate (supply of calcium and sulphate ions) of set regulator the quantity of foil like AFm phases decreases and ettringite is formed (compare Fig. 9A–H). Based on previous investigations [27] and spectrometric analysis by EDX we describe the foil like phases as AFm.

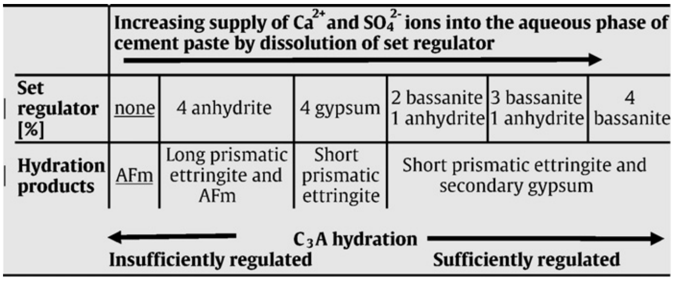
Additionally to ettringite, at high set regulator dissolution rate, crystallisation of secondary gypsum is detected. By ESEM investigations large secondary gypsum crystals are unambiguously identified by their characteristic crystal shape. These crystals are approximately 10–30 µm long and 2–5 µm thick (Fig. 9C). In the sample, containing 4% bassanite as set regulator, those gypsum crystals were first found after 15–20 min of hydration. The period of gypsum formation coincides with the time at which a torque maximum is measured (curve “4% bassanite” in Fig. 8). Therefore we conclude that the torque maximum (minimum in fluidity) is caused by crystallisation of secondary gypsum.

An additional effect of increased set regulator dissolution rate is that the aspect ratio (length/thickness) of ettringite crystals decreases. It was shown by [28] that this effect arises because the supersaturation of the cement paste with respect to ettringite increases. Long prismatic ettringite (aspect ratio >5) is observed if the supersaturation degree for ettringite falls below the value of approx. 8 [28].

AFm phases indicate that C_3A hydration is insufficiently retarded [29]. In contrast the occurrence of secondary gypsum together with ettringite (in samples with 2, 3 and 4% bassanite) shows that excess of calcium and sulphate ions are supplied by set regulator with a high dissolution rate. Thus a maximum retardation of C_3A hydration is achieved (i.e. hydration degree of C_3A is minimised).

ESEM investigations revealed that short prismatic ettringite coexists with secondary gypsum and that long prismatic ettringite

Table 6
Formation of hydration products in dependence of Ca^{2+} and SO_4^{2-} ions supply by set regulator within first hour of hydration



	Increasing supply of Ca^{2+} and SO_4^{2-} ions into the aqueous phase of cement paste by dissolution of set regulator →					
Set regulator [%]	none	4 anhydrite	4 gypsum	2 bassanite 1 anhydrite	3 bassanite 1 anhydrite	4 bassanite
Hydration products	AFm	Long prismatic ettringite and AFm	Short prismatic ettringite	Short prismatic ettringite and secondary gypsum		
	← Insufficiently regulated		C_3A hydration		→ Sufficiently regulated	

coexists with AFm (Fig. 9C–H). Thus it is followed that long prismatic ettringite indicates that the calcium and sulphate ion concentration in the cement pastes is on a lower limit. Calcium and sulphate ion concentrations after 10 min of hydration are shown in Table 5. These results prove that AFm and or long prismatic ettringite are observed if low calcium and sulphate ion concentrations are present. This is in accordance with previous findings [28,29]. A further consequence of the insufficient set regulator dissolution rate may be that the C_3A hydration is insufficiently retarded [28].

Table 6 summarizes the general changes in species and habitus of aluminate hydration products that are formed during the first hour of cement hydration. The starting point of the investigation were the findings presented in an earlier study [28]. There it was found that ettringite morphology varies in dependence of specific surface of clinker, set regulator dissolution rate and superplasticizer addition. In the present study we systematically induced variations of aluminate hydration products by varying only the set regulator composition (i.e. calcium and sulphate ion supply into the aqueous phase of cement paste). By comparing with fluidity measurements it is revealed that the highest fluidity of the pastes was measured in samples with 4% gypsum (Fig. 8). In the respective microstructure the presence of short prismatic ettringite only indicates that the set regulator is sufficient for regulation of C_3A hydration. The absence of AFm phases and secondary gypsum crystals correlates with the highest fluidity of the paste.

Microstructural investigations of hydrating clinker after 10 min of hydration with or without addition of 4% anhydrite show that AFm phases envelope most of the cement particles (Fig. 9A). Thus, a continuous network is built up (Fig. 9D) that connects cement grains (Fig. 9E) and can cause flash set of the paste. Ettringite is rarely observable at this stage of hydration. In contrast, after 2 h of hydration and shearing in the viscometer the microstructure of this paste is dominated by long prismatic ettringite (Fig. 9F, G). This indicates that the AFm network structure is destroyed mechanically and or by reaction of AFm phases to ettringite (due to increasing calcium and sulphate ion supply by subsequent dissolution of anhydrite).

3.3. Development of specific surface area (SSA) of cement during hydration (N_2-BET)

Specific surface area of cements after hydration periods of 30 and 120 min in dependence of viscometer torque (fluidity) are shown in Fig. 10. For clarification Table 7 displays the set regulator composition for labelled data points in Fig. 10. Generally, due to progressing hydration an increase in SSA of cement is detected.

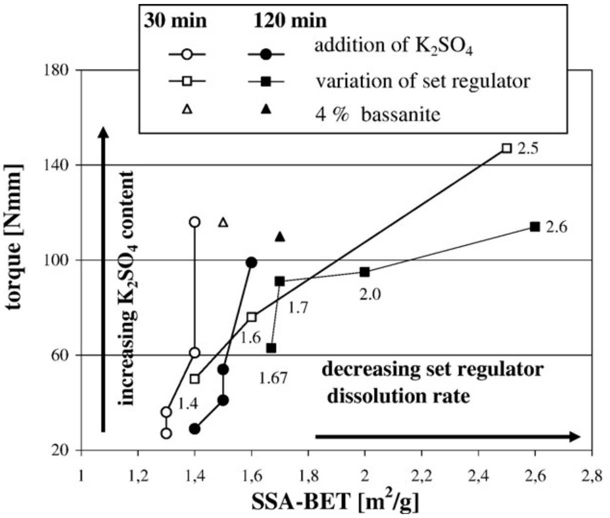


Fig. 10. Viscometer torque of cement pastes after 30 and 120 min of hydration in dependence of SSA, set regulator dissolution rate and potassium sulphate content. Set regulator composition for individual samples is given in Table 7. SSA of unhydrated cement = 0.9 m^2/g.

Table 7
SSA (BET) of hydrated cement in dependence of set regulator and hydration period

Set regulator [wt.%]	SSA (BET) [m^2/g]	
	30 min	120 min
4 gypsum	1.4	1.7
3 bassanite, 1 anhydrite	1.6	1.7
2 bassanite, 1 anhydrite	1.7	2.0
4 anhydrite	2.5	2.6

Furthermore, the results show that by increasing the amount of potassium sulphate, i.e. increased quantity of syngenite, the increase in SSA is negligible but the loss in fluidity is high. Similar effects were observed for crystallisation of secondary gypsum. In contrast, samples with increasing set regulator dissolution rate (i.e. increasing supply of calcium and sulphate ions) develop the SSA that is inversely correlated with fluidity of the pastes. The reason is that the formation of many thin, foil like AFm phases has a marked influence on SSA. In contrast, the contribution of large secondary gypsum and syngenite crystals to SSA is marginal.

4. Discussions

Results of the present study clearly illustrate that if significant quantities of secondary gypsum and syngenite are formed during cement hydration, a loss in fluidity (maximum in torque) is detected. The measured torque maximum correlates very well with the time of syngenite respective gypsum formation. If the formed mineral quantity diminishes the fluidity of the paste, depends on the starting consistency, i.e. water-to-cement ratio etc. For the investigated cement 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. The fluidity of cement A (CEM I 42.5 R) with lower specific surface area (fineness) than cement B, is significantly decreased by the formation of 2.5 wt.% syngenite. For cement A lower syngenite contents could not be detected, because cement composition is unsuitable for XRD analysis [24] on salicylic acid methanol extraction residues (high iron content of cement).

Present models describe that—due to the high ionic strength in the aqueous phase of cement pastes—particles are always flocculated/coagulated [13]. Furthermore it is known that the flocculated state can be transferred into a dispersed state by application of shear forces (stirring) or by addition of superplasticizers. The dispersion of cement particles improves the fluidity of the cement paste. Results of the present investigation have shown that additionally the quantity and morphology of the formed hydrate phases influence the fluidity of cement pastes. It was shown that even small quantities of long prismatic crystals decrease the cement paste fluidity. Furthermore the influence of increasing ionic strength of the aqueous phase on fluidity of cement pastes was compared with the effect of long prismatic crystals.

It was found that increasing the ionic strength (by addition of sodium sulphate) in cement pastes had a comparatively minor influence on fluidity.

Another cause for diminished fluidity in the presence of high alkali sulphate content might be an accelerated hydration of clinker phases induced by increased pH [6].But only addition of 0.29 M Na_2SO_4 solution to cement B leads to a significant increase in torque after 10 min of hydration. According to previous work [26] and investigations of that sample by ESEM no additional hydration products like gypsum are formed. Furthermore results of XRD-Rietveld analysis showed that after 10 min of hydration the variation of C_3A content in cement pastes with increasing alkali sulphate content was smaller than 1 wt.%, i.e. within standard deviation of measurement. Thus it is not assumed that variation in C_3A consumption is responsible for variation in fluidity. These results prove 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 viscometer measurements of cement A were halted after 40 min and restarted after 50 min (Figs. 1 and 7). The magnitude of the torque maximum after restart is approx. ≤10 N mm for all investigated cement pastes. This is always lower than the maxima caused by syngenite formation within the first 10 min of hydration (Fig. 1). Thus we showed again, that the formation of long prismatic crystals affects the cement paste fluidity more significant than increased ionic strength and the following variation in flocculation/coagulation. Furthermore it is deduced that after 40 min of hydration, the precipitation rate of syngenite is marginal as compared to the very first minutes of hydration. Results of quantitative XRD analysis confirmed that from 10 min to 2 h of hydration syngenite content is not significantly increased.

For both cements it was shown that at high syngenite content a significant gain in fluidity is achieved by continuous shear of the paste in the viscometer (at constant rotation speed). General rheological models for suspension indicate that two competing processes induce the minimum and subsequent gain in fluidity during the first 20 min of hydration: A) an increasing formation of hydrate phases [23] and B) the movement of particles (for example hydrate phases) in the sheared suspension [30–32]. For process A) it is known that with increasing asymmetry of particles (from spheroid to rod like) the viscosity (fluidity loss) of a suspension increases [33]. For B) according to the rheological models it is expected that elongated (long prismatic) particles rotate into the shear direction [30,32]. The formation of a preferred orientation of elongated particles in the shear flow results in fluidity gain. Fig. 11 illustrates the process of alignment of long prismatic crystals (like gypsum or syngenite) in simple shear conditions of cement paste. If the 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 minimal. Continuous shear leads to rotation of syngenite and gypsum crystals. Thereby a preferred crystal 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 long prismatic crystals affects not only the viscosity but also the yield stress of suspensions [32,33]. Previous investigations [21] 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 [21]. Additionally it was shown that the concrete yield stress is increased by potassium sulphate concentration and that already the formation of 1 wt.% syngenite has a marked influence on fluidity (yield stress and viscosity) of the investigated cement paste.

Another determining factor for fluidity of cement pastes is the set regulator (calcium sulphate) dissolution rate (supply of calcium and sulphate ions to the aqueous phase of cement paste). Results of this and one previous study [28] have shown that an adequate supply of calcium and sulphate ions into the aqueous phase of cement pastes is necessary to ensure that short prismatic ettringite is formed. Results of the present investigation revealed that a maximum fluidity was achieved in the cement paste with short prismatic ettringite. Whereas the presence of long prismatic ettringite, AFm phases and secondary gypsum caused a fluidity decrease. Long prismatic ettringite and AFm phases are formed if the dissolution rate of set regulator are low. Additionally the existence of AFm phases indicates that C_3A hydration is not sufficiently retarded. According to [19,28] this results in an increased C_3A hydration degree and thereby a reduced fluidity. Therefore in cement pastes with long prismatic ettringite the fluidity is decreased as a result of both factors, inadequate ettringite habitus and insufficiently retarded C_3A hydration.

Furthermore it was shown that SSA of hydrating cement increases if set regulator dissolution rate is decreased. A correlation between SSA and viscometer torque (fluidity) exists for samples with very low dissolution rate of set regulator. In contrast minor increase in SSA and no correlation to fluidity was found in pastes containing syngenite and secondary gypsum. Those crystals were shown to be comparatively large and therefore their contribution to the SSA is low.

Nevertheless compared to unhydrated cement the SSA was always shown to be increased by hydration. Also in dependence of mineralogical composition of cements (set regulator composition), significant variation of the SSA during hydration may occur. This finding is particular important not only with regard to fluidity of pastes but also within the light of measuring of superplasticizers adsorption on different cements.

5. Conclusions

The influence of hydration products on cement paste fluidity was studied. By controlling the potassium sulphate and set regulator dissolution rate the relationship between the formation of syngenite, AFm, ettringite, gypsum and fluidity of the paste was investigated.

Results show that immediately after addition of the mixing water, the fluidity is decreased by formation of syngenite or AFm phases. After a hydration period of 15–20 min a fluidity decrease is caused by gypsum crystallisation.

General models describe the fluidity of cement paste by properties of a coagulated/flocculated suspension under the influence of shear (mixing energy) on the floc structure. The work presented here extends this view for the case of formation of long prismatic hydrates like syngenite or gypsum. It was shown that in the presence of those hydrates the application of shear energy (mixing) increases the fluidity of cement paste by the development of a preferred crystal orientation.

As to the formation of AFm phases the fluidity improvement during shearing and hydration is explained by two effects: firstly the AFm network structure that connects cement particles is mechanically destroyed by the applied shear forces; secondly with progressing hydration time the initially formed AFm phases might be replaced by ettringite. This is possible because over time anhydrite is slowly

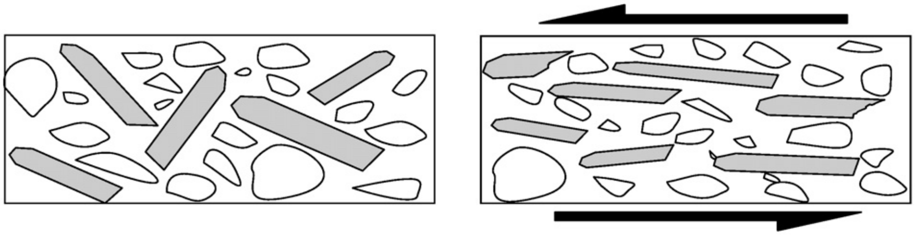


Fig. 11. Alignment of long prismatic crystals like syngenite and secondary gypsum in the shear direction (indicated by arrows); development of a preferred crystal orientation.

dissolving, i.e. calcium and sulphate ions necessary for the formation of ettringite are only subsequently released. Obviously, the formed, discrete ettringite crystals are not able to envelope and connect clinker grains with the same efficiency as AFm phases. Thus a better dispersion of the cement particles is achieved and fluidity of the paste is increased.

Furthermore, it is known that the occurrence of AFm phases indicates an insufficiently retarded C_3A hydration. In contrast, secondary gypsum indicates an excess supply of calcium and sulphate ions into the aqueous phase of cement pastes by the added set regulator. By the present investigation it is indicated that, in the absence of AFm phases or secondary gypsum, the occurrence of long or short prismatic ettringite is a further indicator towards insufficient or sufficient C_3A retardation respectively. According to general models for rheology of suspensions it is expected that compared to short prismatic ettringite the long prismatic crystal habitus is always related with a diminished fluidity. Nevertheless the total impact of ettringite morphology is always difficult to assess because as shown by the present investigation the occurrence of long prismatic ettringite was accompanied by fluidity decreasing AFm phases.

Also it was shown that the SSA of hydrating cements varies greatly. It is expected that this variation is more significant for cements with low set regulator dissolution rate and low alkali content. In those cements the SSA correlates with the fluidity.

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