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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