The shear-thickening effect of meta muscovite in cementitious systems

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Abstract

Calcined clays as supplementary cementitious material (SCM) for ecologically optimized concretes exhibit a high water demand and therefore require the usage of superplasticizers in cementitious systems to enable sufficient low water-to-binder (w/b) values that are relevant in application. Mixed layer clays, which are interesting as raw material for calcination procedure, consist of different types of phyllosilicates and inert components, e. g. quartz at different percentages [1]. The most common phyllosilicates are kaolinite, montmorillonite, illite and mica/muscovite [2]. The latter one was calcined and its meta phase (meta muscovite) was investigated in cementitious systems.

This paper summarizes the results of a study undertaken to evaluate the rheological influence of meta muscovite as replacement (20 wt. %) for an ordinary Portland cement (OPC). Measurements on viscosity with and without superplasticizer at different w/b values are compared and the development of these rheological properties over time are considered.

The results highlight the rheological features encountered when a polycarboxylate ether-based superplasticizer is added to a meta muscovite blended OPC to the point of a complete change from a pseudoplastic to a shear-thickening (dilatant) cementitious paste at a w/b value of 0.50.

Additionally it is stated that workability of calcined clay blended cement cannot be defined simply over flow tests, but it has to be looked at more rheological parameters, such as viscosity and shear stress.

Keywords: Calcination; polycarboxylate ether; shear-thickening effect; supplementary cementitious material; viscosity.

1. Introduction

Due to their low carbon dioxide emissions during calcination, calcined (thermally activated) clays represent a potential sustainable material to meet the future demand of supplementary cementitious materials (SCMs) by cement industry. With a widespread abundance and large deposits worldwide, calcined clays are among the most promising SCMs, especially with their beneficial effects on durability of concrete, e. g. pozzolanic activity and filler effects [3–5].

Apart the side effect of a high water demand, substitution of ordinary Portland cement (OPC) by calcined phyllosilicates can create a very interesting rheological performance of blended cement.

The knowledge of rheological parameters of cement-based products is of prominent importance to predict their workability in different fields of application like pumping, spreading, molding and compacting processes. The complexity of the rheological behavior is much more pronounced since the combined use of supplementary cementitious materials and chemical admixtures such as superplasticizers is increasing [6–9].
The aim of this study is to assess meta muscovite as non-negligible component in calcined clays as SCM in combination with a methacrylate ester based polycarboxylate ether (PCE) superplasticizer as rheology modifying admixture.

2. Materials and methods

2.1. Materials

Cement
An OPC CEM I 42.5 R from Schwenk Zement KG (Allmendingen, Germany) was used. Its mineral phase composition is summarized in **Table 1**.

Table 1. Phase composition of the CEM I 42.5 R sample as determined by Q-XRD using *Rietveld* refinement.

Mineral phase	wt. %
C_3S, m	56.5
C_2S, m	15.6
C_3A, c	5.5
C_3A, o	2.0
C_4AF	9.9
CaO	0.6
MgO	0.4
Anhydrite	1.7
Dihydrate*	3.3
Calcite	3.2
Quartz	0.5
Dolomite	0.8
Total	100.0

* determined by thermogravimetry

Meta muscovite
A muscovite was calcined in a lab muffle kiln at 800 °C for one hour. The temperature was chosen according to the dehydroxylation temperature obtained *via* differential thermal analysis and optimal solubility of Al- and Si-ions in alkaline solution to gain the highest pozzolanic activity. During calcination, the OH^- bands dehydroxylate from interlayers between silicon tetrahedrons and aluminum octahedrons and the muscovite transforms at this temperature range to a meta phase: meta muscovite [10]. The meta muscovite contains 80.8 wt. % muscovite (high-temperature modification) and 19.2 wt. % amorphous phases.

Important physical characteristics are given in **Table 2**. The substitution rate of cement was set at 20 wt. %.

Table 2. Physical parameters of meta muscovite.

Parameter	
Particle density [g/cm^3]	2.8
Specific surface area [m^2/g]	11.8
Water demand [wt. %]	55.4
Average particle size (d_{50} value) [µm]	19.2

Superplasticizer

A lab-synthesized PCE superplasticizer (MAA-113MPEG (6:1)) was selected to investigate its influence on the rheological behavior of pastes of pure meta muscovite, neat cement and blended cementitious systems. A methoxy poly(ethylene glycol) (MPEG) methacrylate ester with a long side chain (number of ethylene oxide units ($n_{(EO)}$ = 113) as macromonomer was copolymerized with methacrylic acid (MAA). The MAA:MPEG ratio is 6:1 and its solid content is around 35 %. The structure of the PCE is shown in **Figure 1**.

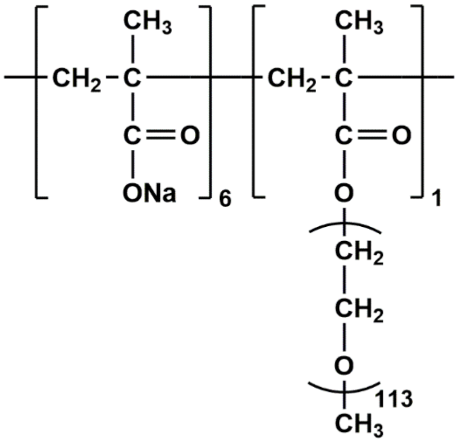

Figure 1. Chemical composition of MAA-113MPEG (6:1).

2.2. Methods

Rheological measurements

A rotational viscometer, *Brookfield* Dial Reading Viscometer (*Brookfield* Engineering Inc., Model HA) with disk spindle RV-4 was used to determine the viscosity of blended cement under ambient temperature (20 ± 1 °C). The spindle number was selected in accordance with the properties of the samples to get all readings up to at least 10 % of the scale due to accuracy and all readings within the scale.

The first measurements were taken two minutes after the spindle was immersed in each sample and in total six minutes after the first contact of cement and/or meta muscovite with water. The dial readings were recorded in ascending and descending order at 1, 2, 5, 10, 20, 50 and 100 revolutions per minute (rpm) taking the mean dial readings at different speeds for the calculation of the viscosity. Each rotation speed was kept for one minute to guarantee an equilibration of the paste.

Time dependent measurements were followed up over five hours in time intervals of 15 to 30 minutes at a constant rotation speed of 50 rpm. To prevent water evaporation, the pastes were covered with a wet towel between the measurements. Two minutes prior to each measurement, the pastes were stirred by hand to maintain a homogenous suspension. Two different water-to-binder ratios (w/b ratios) were selected: 0.50 and 0.65.

The dosages of the superplasticizer were chosen as to achieve a stable, homogeneous cement pastes over the whole measuring period, e.g. no settling or bleeding effects.

3. Results and discussion

3.1. Viscosity of cement pastes substituted with meta muscovite

With the addition of 20 wt. % of meta muscovite at constant w/b ratios, the blended cement paste alters its rheological behavior completely compared to neat cement paste. Firstly, the cementitious system cannot be fluidized anymore to a compact paste with the addition of water at a w/b ratio of 0.50 due to the very high water demand of meta muscovite of 55.4 % [11]. In order to overcome the loss in fluidity, MAA-113MPEG (6:1) is added at an appropriate dosage of 0.25 % bwob to achieve a similar viscosity at 1 rpm both in neat cement paste and the blended cement paste. Up to a rotational speed of 5 rpm, these two cementitious systems behave quite similar in viscosity, while with increasing speed the meta muscovite/cement system does not reach as low viscosity values (2900 mPa·s compared to 5700 mPa·s) as in neat cement paste. However, both binder systems exhibit pseudoplastic flow characteristics.

Surprisingly, with an increasing dosage of 0.30 and 0.35 % bwob of superplasticizer, the rheological behavior of the blended cement shows a serious change. Here, the paste behaves as a shear-thickening fluid, meaning that the apparent viscosity increases with ascending rotational speed (**Figure 2**).

In order to evaluate the influence of the w/b ratio on the change in rheology, similar measurements were taken out at a w/b value of 0.65. For a roughly identical viscosity (~ 4000 mPa·s) at 50 rpm only small amounts of MAA-113MPEG were necessary (0 – 0.10 % bwob). As it is shown in **Figure 3**, the cement paste blended with meta muscovite exhibit a shear-thinning (pseudoplastic) behavior, meaning that at a higher water amount available for dispersing the binder particles, the very pronounced change to a shear-thickening flowability (**Figure 2**) was not observed anymore.

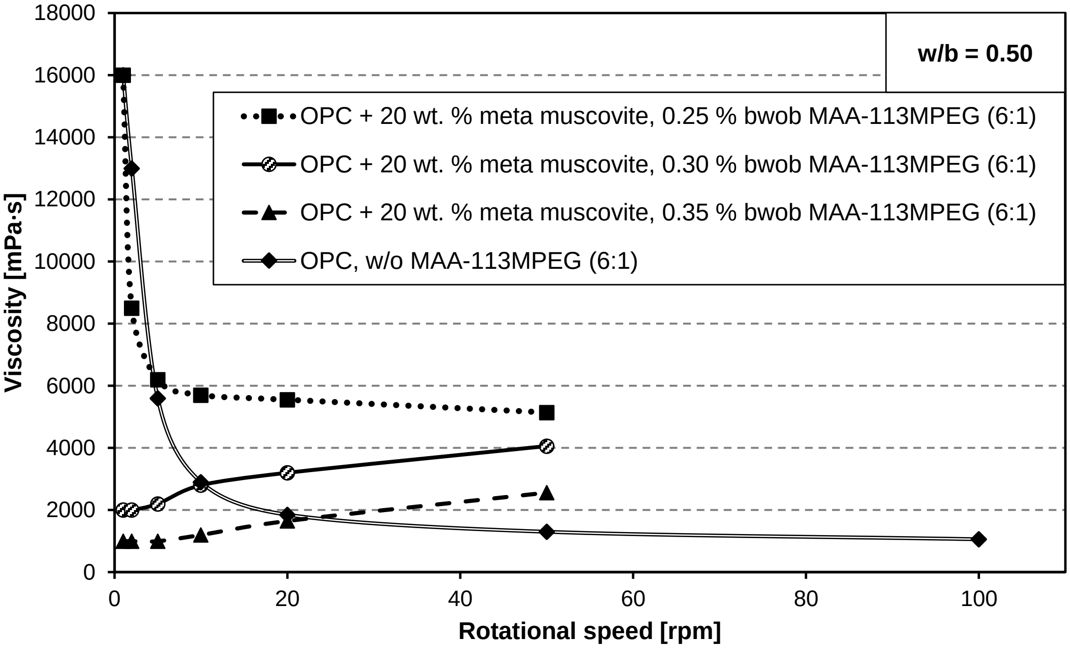

Figure 2. Viscosity curves of OPC blended with 20 wt. % meta muscovite and admixed with various dosages of MAA-113MPEG (6:1) at a w/b ratio of 0.50.

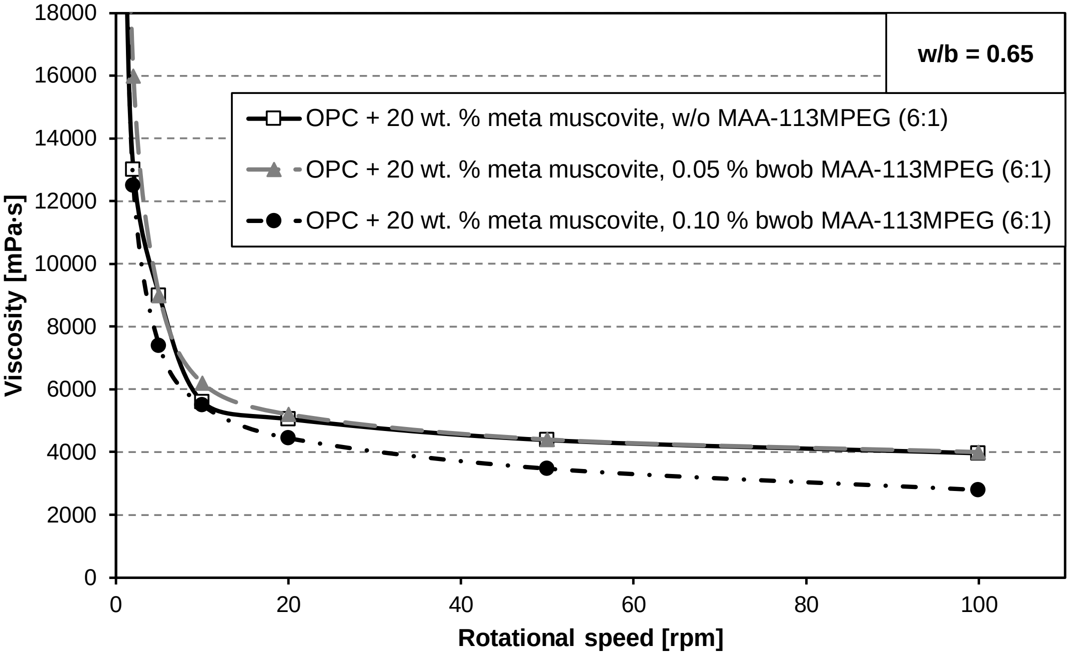

Figure 3. Viscosity curves of OPC blended with 20 wt. % meta muscovite and admixed with various dosages of MAA-113MPEG (6:1) at a w/b ratio of 0.65.

The results allow to state that the shear-thickening response is dominant in highly concentrated binder suspensions and at a sufficient high content of superplasticizer. As in further investigations the dilatant behavior was not observed in presence of shorter side chains ($n_{(EO)}$ = 45), shear-thickening effect seems to ask for a long side chain in the PCE. Hence, the steric dispersing effect seems to promote the occurrence of shear-thickening behavior. This might be attributed to the increasing disorder state due to the presence of long polymer chains that additionally favor cluster formation [12, 13].

3.2. Time dependent viscosity of cement pastes blended with meta muscovite

The development of the viscosity of blended cement pastes over time pointed out another extraordinary result. While at a higher w/b ratio the viscosity increases almost linearly in between of five hours and independently of the added amount of PCE, the viscosity at a w/b ratio of 0.50 decreases between 15 and 90 minutes for both dosages (0.25 and 0.30 % bwob) of MAA-113MPEG (6:1). After three and five hours respectively, the viscosities are comparable to the systems with a w/b value of 0.50 (**Figure 4**).

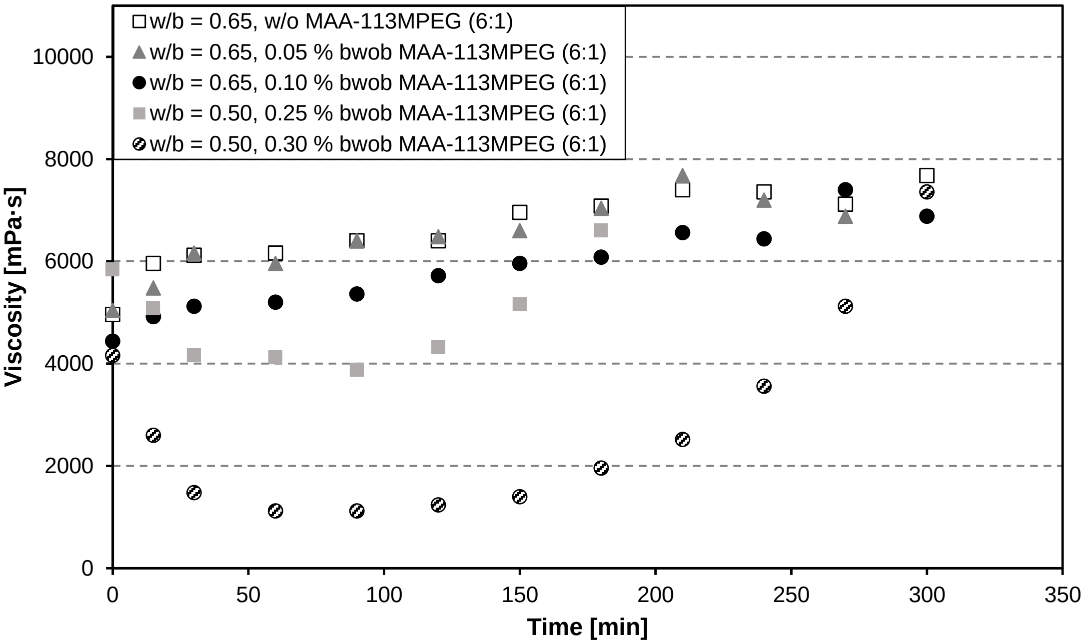

Figure 4. Time dependent development of the viscosity of OPC blended with 20 wt. % of meta muscovite admixed with various dosages of MAA-113MPEG (6:1) at w/b ratios of 0.50 and 0.65.

Further tests with pure meta muscovite in synthetic cement pore solution and with neat cement paste admixed with PCE revealed no decrease in viscosity within the observed period. In these pastes, the viscosity stays constant for meta muscovite, while the increase in viscosity in neat cement paste is explained by the stiffening effect during the hydration process of the clinker phases.

4. Conclusion

The investigations performed on meta muscovite revealed that when thermally activated phyllosilicates are components in SCM, many aspects need to be considered. It can be summarized that for meta muscovite the rheological behavior is mainly depending on an interplay of

- w/b value
- type of superplasticizer and
- dosage of superplasticizer.

Beside the usual focus on reactivity of calcined phyllosilicates as SCM, it is urgently necessary to understand the interaction between their single components and superplasticizers and their unique behavior regarding the rheology in cementitious systems. It is necessary to test different kinds of superplasticizers (e. g. various types of polycarboxylates, polycondensates, small molecules or phosphate based comb polymers) on their impact of rheological parameters. Slump flow tests should be performed to get a link between viscosity and flowability of blended cement pastes.

For further investigations, it is also indispensable to use a more appropriate rheometer for measurements determining wide-ranging rheological parameters like yield stress yield point and shear rate. As final aim, the rheological behavior of different calcined phyllosilicates at varying substitution rates should be described with well-known or even unknown models and the transfer to mortar and concrete should be evaluated. Based on this knowledge, purpose-designed admixtures might be required which open a wide field of research for the future.

5. Acknowledgement

The authors wish to express their sincere gratitude to Deutsche Forschungsgemeinschaft (DFG), Bonn, Germany for the financial support under the grants PL 472/11-1 and TH 1383-1 entitled “Ecological and energetic optimization of concrete: Interaction of structurally divergent superplasticizers with calcined clays”.

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