

~~Accessibility of a Calcined Mixed Layer Clay for Amphoteric Superplasticizers and Its Application as Supplementary Cementitious Material~~

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Abstract. This study highlights the suitability of amphoteric (zwitterionic) polycarboxylate-based superplasticizers for a naturally occurring mixed layer clay used as pozzolanic cement substitute after calcination. After a successful synthesis, dispersing performance tests reveal that amphoteric superplasticizers are a promising type of superplasticizer to address both calcined clays and cement. Tailor-made terpolymers can be applied to vary the initial slump by integration of different ratios of cationic monomer. Furthermore, heat flow calorimetry tests with amphoteric superplasticizers point out a less pronounced retardation in cement hydration compared to a standard anionic polymer. Zwitterionic superplasticizers are seen as potential alternatives for common anionic superplasticizers, especially for the advancing replacement of cement clinker with calcined clays of various mineralogical composition. Calcined mixed layer clays are particularly promising as supplementary cementitious materials (SCMs) as they can be fluidized at low dosages of superplasticizers comparable to cement.

Keywords: Amphoteric polymers, cement hydration, dispersing performance, polycarboxylate ether, workability.

1 Introduction

Optimizing the ecological and energetic properties of concrete asks for the use of pozzolanic cement constituents instead of ordinary Portland cement clinker [1]. The only type of SCM which is available in sufficiently high amounts nearly all over the world is calcined clay. These thermally activated clays are ascribed to have an appreciable potential to contribute to the reduction of cement derived carbon dioxide emissions as well as of thermal energy required during processing [2-4].

However, cements substituted with calcined clays suffer from a very high water demand and consequently evoke a limited workability of mortars and concretes [5]. To overcome this disadvantage and to avoid a loss on mechanical properties and durability when increasing the water-to-binder (w/b) ratio, the addition of superplasticizers is essential [6].

While in literature [7, 8], many studies do not consider the interaction with water-reducing admixtures in the assessment of low-grade calcined clays, the present study reports on a calcined naturally available mixed layer clay as SCM and its accessibility for amphoteric superplasticizers.

Our previous investigations [9] pointed out that the present clay can be dispersed well with anionic polycarboxylate ethers (PCEs) and cationic polymers. Moreover zeta potential measurements suggested that this clay exhibits particles with positive and negative surface charges [10].

Hence, amphoteric (zwitterionic) PCE superplasticizers exhibiting different ratios of anionic/cationic monomer were synthesized, characterized *via* gel permeation chromatography (GPC) and tested in cement blended with this calcined clay on dispersing effectiveness and influence on cement hydration.

2 Materials and Methods

2.1 Materials

Calcined Clay. As clay sample a naturally occurring mixed layer clay was investigated. The raw material originates from a Lias delta layer in Bavaria (Germany). It is composed of approximately 25 wt. % kaolinite and 45 wt. % 2:1 clay minerals (especially mica, illite and chlorite). Quartz and feldspar (around 30 wt. %) are included as inert components. Calcination at 750 °C in a three-part rotary kiln for around 30 minutes results in a material with 61 wt. % amorphous content. The mineralogical composition of the calcined material is summarized in **Table 1**. The calcined clay (CC) exhibits a specific surface (BET surface) area of 3.9 m²/g and a particle density of 2.63 g/cm³.

Table 1. Mineralogical composition of the calcined mixed layer clay sample.

Phase	[wt. %]
Quartz	16.2
Muscovite	2.2
Calcite	0.6
Illite	4.6
Chlorite	0.4
Feldspar	6.0
Secondary silicates	6.3
Hematite	0.6
Ores	1.1
Sulfates	1.6
X-ray amorphous	60.8
Total	100.4

Cement. An ordinary Portland cement (OPC) CEM I 42.5 R from Schwenk Zement KG (Allmendingen, Germany) is used for the production of cements blended with the calcined clay. The *Blaine* value is 2,918 cm²/g, and the particle density is 3.16 g/cm³. Its mineralogical analysis is shown in **Table 2**.

Table 2. Phase composition of the CEM I 42.5 R sample.

Mineral phase	[wt. %]
C ₃ S, m	52.4
C ₂ S, m	19.9
C ₃ A, c	3.3
C ₃ A, o	3.2
C ₄ AF	11.8
CaO	0.7
MgO	0.7
Anhydrite	1.4
Hemihydrate*	1.9
Dihydrate*	1.3
Calcite	1.6
Quartz	0.4
Dolomite	1.4
Total	100.0

* determined by thermogravimetry

Characteristic particle size parameters, i. e. d_{10} , d_{50} and d_{90} values of the CC and the OPC sample are given in **Table 3**.

Table 3. D_{10} , d_{50} and d_{90} values of the OPC and the CC.

Sample	[μm]		
	d_{10}	d_{50}	d_{90}
CC	4.0	13.2	37.0
OPC	1.5	18.5	48.7

The particle size distribution of the OPC and the calcined mixed layer clay was measured *via* laser granulometry and is presented in **Figures 1 and 2**.

CC exhibits a unimodal distribution. For the OPC, the volume of finer particles is larger than that of CC, but it also includes coarse particles (higher d_{90} value compared to CC).

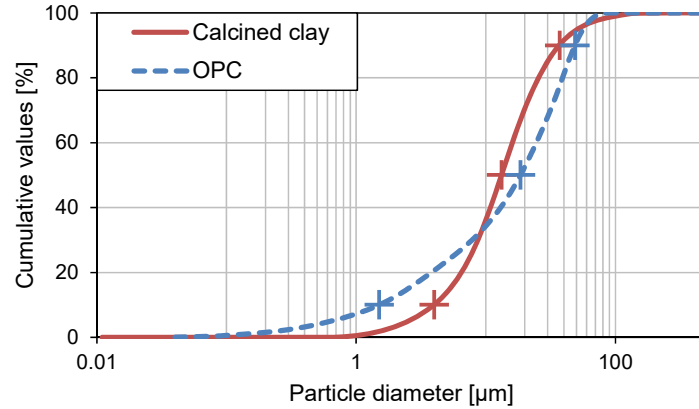


Fig. 1. Cumulative particle size distribution of the calcined clay and OPC samples (d_{10} , d_{50} and d_{90} values are marked with a cross).

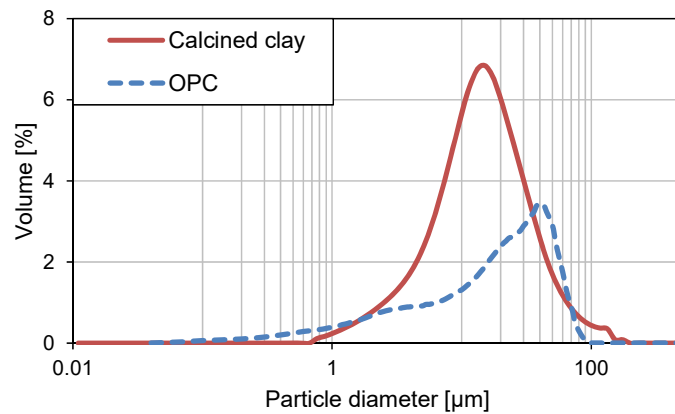


Fig. 2. Frequency distribution of the calcined clay and OPC samples.

Superplasticizers. As amphoteric (zwitterionic) superplasticizers, four terpolymers were prepared *via* aqueous free radical copolymerization of the monomers methacrylic acid (MAA), MPEG-methacrylate macromonomer (ω -methoxy polyethylene glycol methacrylate ester with a chain length (n_{EO}) of 45) and 3-trimethylammonium propyl methacrylamide chloride (MAPTAC). The polymerization was initiated with ammonium peroxodisulfate and controlled with 3-mercaptopropionic acid as chain transfer agent. After neutralization with sodium hydroxide solution, the polymers were obtained as yellowish and slightly viscous polymer solutions with a solid content of $\sim 25\%$.

For comparison, a standard anionic PCE (MAA-45MPEG (6:1)) was investigated. The chemical structures of the polymers are shown in **Figure 3**.

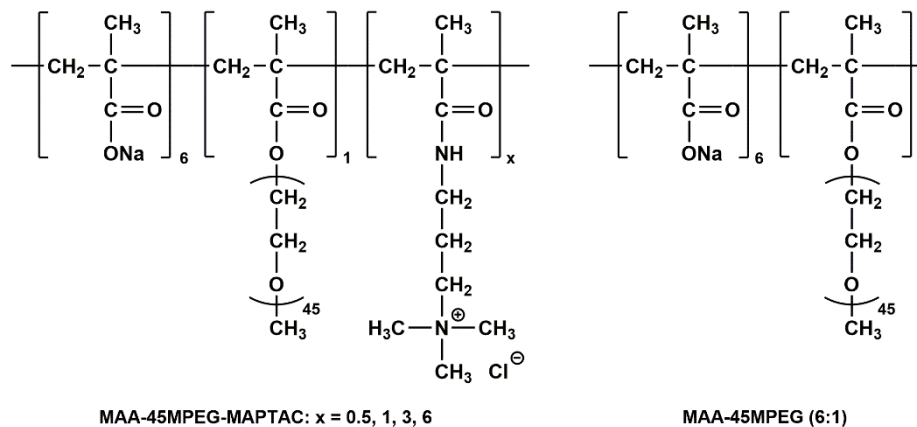


Fig. 3. Chemical structures of the synthesized amphoteric PCE samples and the anionic reference polycarboxylate ether.

All terpolymers were characterized by gel permeation chromatography. The molecular weights (M_w and M_n) and polydispersity indexes (PDI) of the polymers obtained from these measurements are summarized in **Table 4**.

Table 4. Molecular properties and macromonomer conversion of the synthesized polymers.

Polymer sample	M_w [g/mol]	M_n [g/mol]	PDI	Conversion [%]
MAA-45MPEG-MAPTAC (6:1:6)	15,000	9,700	1.5	76.9
MAA-45MPEG-MAPTAC (6:1:3)	18,000	9,600	1.9	84.7
MAA-45MPEG-MAPTAC (6:1:1)	22,000	11,000	2.0	89.1
MAA-45MPEG-MAPTAC (6:1:0.5)	21,000	9,400	2.2	86.0
MAA-45MPEG (6:1)	14,900	7,400	2.0	91.9

2.2 Methods

Dispersing Performance of Synthesized Polymers. Dispersing effectiveness of the synthesized superplasticizer samples in CC, neat OPC and OPC blended with CC suspensions was assessed *via* a modified (adapted from DIN EN 1015-3 [11]) mini slump test using a *Vicat* cone (bottom diameter: 8.0 cm, top diameter: 7.0 cm, height: 4.0 cm). The substitution rate for the cement was set at 20 wt. %.

In this test, the cone was filled with the paste and the spread diameter was recorded after removing the cone. The average value of two spread diameters perpendicular to each other was reported as the test result. The w/b ratios of the pastes without polymer was set to give a spread flow of 18 ± 0.5 cm and was 0.77, 0.48 and 0.55 for pure CC, neat cement and blended cement paste, respectively. At those w/b ratios, the dosages of the superplasticizers required to reach a spread flow of 26 ± 0.5 cm were determined.

Isothermal Heat Flow Calorimetry. Hydration kinetics were monitored by isothermal heat flow calorimetry (TAM AIR, Thermometric, Järfälla, Sweden) at 20 °C. All pastes of the blended cement (OPC:CC 80:20) were prepared from 4.0 g of binder and 2.2 g of distilled water ($w/b = 0.55$). The dosages of the superplasticizers were those which were required to achieve a spread flow of 26 ± 0.5 cm in the mini slump tests in order to ensure comparable rheological properties and avoid segregation of the paste during the hydration process. The heat release during hydration was reported over a period of 48 hours.

3 Results and Discussion

3.1 Dispersing Effectiveness of Amphoteric Superplasticizers

Generally, in the calcined clay suspension always the highest dosages of the novel superplasticizers were required to achieve a spread flow of 26 ± 0.5 cm when compared with neat cement or the OPC/CC blend. In light of this it was quite surprising that in the blended cement, lower or the same dosages of the amphoteric superplasticizers were required to achieve the same spread flow as in the neat cement paste (**Figure 4**).

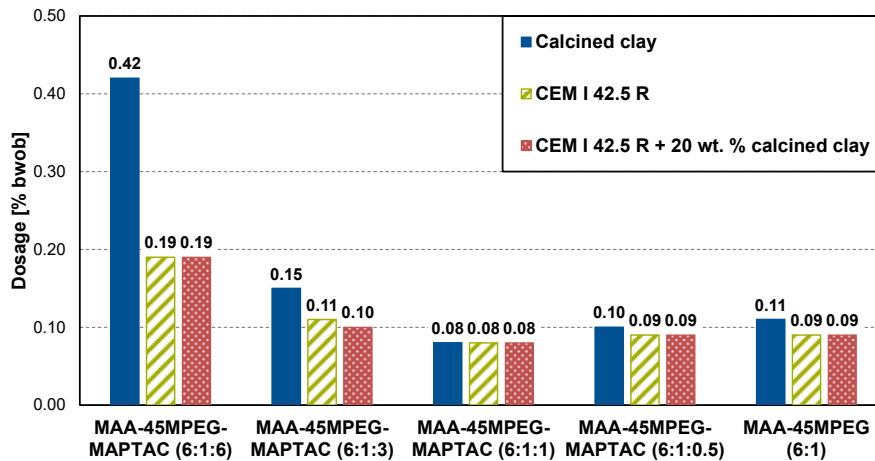


Fig. 4. Dosages of synthesized superplasticizers required to obtain a target slump flow of 26 ± 0.5 cm in calcined clay, cement and an 80:20 blend of cement and calcined clay.

Among the MAPTAC-modified samples, polymer MAA-45MPEG-MAPTAC synthesized at a molar ratio of 6:1:1 performs best, implying that an anionic to cationic charge ratio of 6:1 seems to be the most efficient composition for these terpolymers.

3.2 Impact of Amphoteric Superplasticizers on Cement Hydration

The effect of the synthesized amphoteric terpolymers on the hydration of the blended cement was studied *via* isothermal heat flow calorimetry (**Figure 5**). When the amphoteric comb polymers are added, no (e. g. sample MAA-45MPEG-MAPTAC (6:1:0.5)) or only a slight (~ 2 hours, e. g. sample MAA-45MPEG-MAPTAC (6:1:6)) delay in the induction period was observed indicating no influence on the silicate clinker hydration.

Moreover, for all zwitterionic polymers the deceleration period exhibits a much higher exothermic rate which leads to a shorter period of heat evolution, indicating a faster kinetics of the early hydration compared to an anionic MAA-45MPEG (6:1).

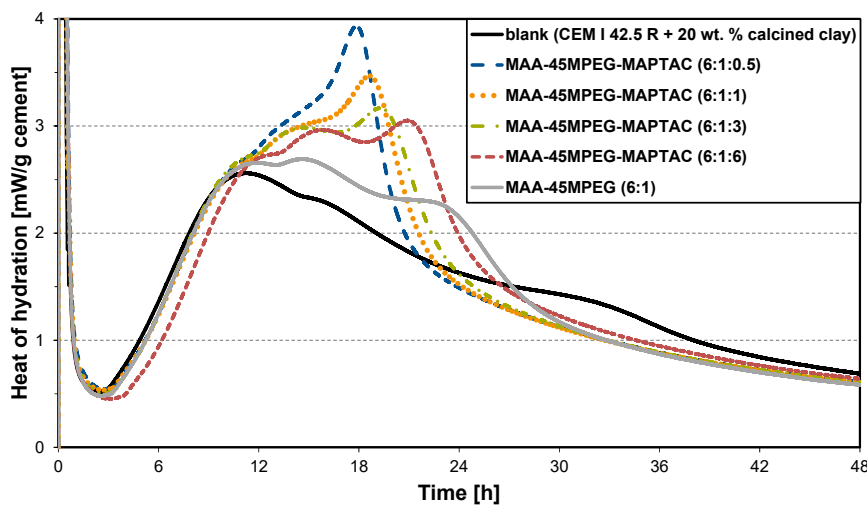


Fig. 5. Heat evolution during hydration of CEM I 42.5 R blended with 20 wt. % calcined clay ($w/b = 0.55$) admixed with superplasticizers (polymer dosage as shown in **Figure 4**).

4 Conclusions

In the present study, four amphoteric comb copolymers composed of methacrylic acid, MPEG macromonomer and MAPTAC as cationic monomer were synthesized and their ability to disperse OPC blended with a calcined naturally occurring mixed layer clay was investigated.

It can be concluded that optimal dispersing effectiveness is achieved at a low content of cationic monomer.

Moreover, the investigations revealed that zwitterionic polymers show no or only a minor retarding effect on early cement hydration and can even shorten the heat evolution period in the first 48 hours compared to conventional anionic polycarboxylates.

The authors are aware that for a better understanding of the influence of a cationic monomer on the dispersing mechanism, adsorption and zeta potential measurements have to be conducted. Moreover, heat flow calorimetry results have to be proven and underpinned by compressive strength measurements.

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