



## Research Paper

# Rheology of calcined illitic and smectitic clays in cement-free aqueous solutions with a focus on ion adsorption and superplasticizer interaction

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## ABSTRACT

Calcined clays (CCs) are a promising supplementary cementitious material to advance decarbonization of cement, even though they are a challenge in rheology. The study focuses on the interaction of CCs, pore solution ions, and superplasticizer to improve rheology with CC. This was done with four illitic and smectitic dominated CCs in cement-free aqueous solutions. Rheometry, infrared spectroscopy, electroacoustic measurements, X-ray diffraction, and water absorption capacity measurements were conducted to investigate superplasticizer intercalation and adsorption, hydration, surface charge, ion adsorption, and rheology. Yield stress increased in synthetic cement pore solution in comparison to deionized water. This was not attributed to hydration products or a change in pH value, but explained by Derjaguin–Landau–Verwey–Overbeek theory (DLVO) due to changed zeta potential and ion concentration. CCs can adsorb anionic superplasticizers onto their negatively charged surface. With calcium addition, their surface charge polarity was reversed, and superplasticizer adsorption increased drastically. Superplasticizer demand seemed independent of sulfate addition, which is contradictory with cement systems. Superplasticizer demand was twice as high for illitic CCs compared to smectitic CCs. Intercalation of superplasticizers and swelling of calcined smectite can be excluded. The results confirmed BET specific surface area as a generally good indicator for superplasticizer demand of CCs, but it is not sufficient for differentiation within similar mineralogy. These findings help to further establish CCs further as an eco-friendly but also workable supplementary cementitious material.

## 1. Introduction

Calcined clays (CCs) are a promising supplementary cementitious material (SCM) that can lower CO<sub>2</sub> emissions by partial replacement of cement (Avet et al., 2019). This gave CCs a focus in the scientific community with conference series such as Calcined Clays for Sustainable Concrete (Sharma et al., 2022) or international technical committees by RILEM (Zunino et al., 2022). Many researchers focus on 1:1 kaolinitic clays. However, available clay resources in regions with a moderate climate, e.g., Germany, contain high amounts of 2:1 phyllosilicates (Maier et al., 2020). By replacing cement with CCs the cement hydration may change due to aspects such as hydration of the aluminate clinker phase C<sub>3</sub>A and sulfate carrier interaction (Maier et al., 2021b), as well silicate clinker phase C<sub>3</sub>S (Sowoidnich et al., 2023), creation of hydration phases on their own (Scherb et al., 2025), impact due to adsorption on CC surfaces (Schmid and Plank, 2021) or dissolution rate of clinker phases (Zunino, 2020).

Besides the benefits in pozzolanic reactivity this also has a challenging impact on the rheology and usually increases the superplasticizer demand (Sposito et al., 2021b), which limits their use due to lower workability of concrete. Therefore, an in-depth understanding of 2:1 dominated CCs and their impact on rheology and superplasticizer demand is required to develop an eco-friendly and workable concrete. Workability is governed by several factors, including ion concentration, superplasticizer adsorption, and interparticle forces, which will be discussed in detail in the following sections.

### 1.1. Ion concentration in cement pore solution

During early hydration, the availability of ions in pore solution depends on several factors: dissolution of clinker phases and solubility of ions from CCs (Beuntner and Thienel, 2016), precipitation reactions, and adsorption mechanics. If hydration consumes more ions than dissolution provides, the ion concentration in the pore solution and

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adsorption on surfaces is reduced, and vice versa. When the precipitation and dissolution rates are constant, the ion surface coverage and pore solution concentration remain constant (Jansen et al., 2018).

The dissolution of the sulfate carrier can be completed within the first 10 min, or it may take up to 8 h, depending on the type and content of the sulfate carrier (Jakob et al., 2019; Maier et al., 2021b). The C<sub>3</sub>A content dissolves partly right at the start of hydration and then rests for the next hours. Other clinker phases usually do not dissolve significantly during the first hours (Jansen et al., 2018).

During early hydration, ettringite forms immediately after water addition. In most in situ X-ray diffraction (XRD) experiments, it can be detected at the very beginning of the measurement (Hesse et al., 2011; Jansen et al., 2012). Gypsum may hydrate as well in the first 10 min. Calcium silicate hydrate (C-S-H) and other phases develop much later (Jakob et al., 2019). Ettringite is known to be the dominant factor for a decrease in the workability of cement pastes (Jakob et al., 2019; Rößler et al., 2008; Zingg et al., 2008).

Kelzenberg et al. (1998) reported that 1 min after mixing, the ion concentrations for calcium ions are quite high, but reduced to a lower value after 10 min and then stay low, more or less constant, for 2 h (Dengler et al., 2024). Jansen et al. (2018) analyzed ion adsorption and pore solution of cement. Most of the dissolved calcium ions are considered to be either adsorbed to surfaces or precipitated in hydration products such as C-S-H (Labbez et al., 2006), leaving only a very low amount of calcium in the pore solution itself. Thus, during initial mixing, enough calcium is dissolved to cover the surfaces of the materials and hydration products. Afterwards, there is a balance in dissolution and precipitation of calcium ions, maintaining the amount of adsorbed calcium ions on surfaces constant at  $\sim 23 \text{ mg}_{\text{calcium}}/\text{g binder}$  and just a minor content in the pore solution (Jansen et al., 2018).

Sulfate ( $\text{SO}_4^{2-}$ ) ion concentration is elevated during initial dissolution (Dengler et al., 2024; Kelzenberg et al., 1998). Afterwards, the sulfate ions adsorb on surfaces ( $15 \text{ mg SO}_3/\text{g binder}$ ), such as ettringite (Medala et al., 2011) or on C-S-H phases covered with calcium (Labbez et al., 2006). Sulfate in the pore solution decreases continuously until the sulfate depletion (Jansen et al., 2018; Labbez et al., 2006).

Calcined clays exhibit a negative zeta potential in alkaline solutions, which can range from -1 mV to -50 mV depending on the CC (Sposito et al., 2021a). This allows positively charged calcium ions to adsorb onto their surface, making the CC surfaces more positive (Li et al., 2021). Sulfate ions can adsorb onto the calcium-covered surfaces, decreasing the zeta potential again (Maier et al., 2021b; Maier et al., 2022). The surface coverage of calcium ions leads to an increase in yield stress, due to ion-ion correlation forces, as postulated by (Demeusy et al., 2023).

## 1.2. Superplasticizer

Superplasticizers (SP) are used to improve the workability of cementitious systems. Their working mechanisms are dependent on many factors, including the ion content in the pore solution. The effect of ion adsorption on the flowability and its interaction with superplasticizer adsorption in cement paste was investigated (Yamada et al., 2001). The separate addition of NaCl and Na<sub>2</sub>SO<sub>4</sub> to cement paste with SP decreases the flowability. Adding CaCl<sub>2</sub> to a system with cement paste, superplasticizer, and sulfate ions has the following effects: A reduction of sulfate in pore solution, an increase of SP adsorption and an improved workability. These effects can be reversed with Na<sub>2</sub>SO<sub>4</sub> addition. SPs and sulfate ions are adsorbing competitively (Qianping et al., 2014; Yamada et al., 1998). Only adsorbed superplasticizers improve workability (Yamada et al., 2001).

Polyacrylate ethers (PCEs) generally have an anionic backbone and adsorb on positive surfaces (Flatt and Schober, 2012; Hanehara and Yamada, 2008). Ettringite exhibits a high specific surface area and a positively charged surface (Medala et al., 2011), making it a preferred surface for superplasticizer adsorption (Lei et al., 2022b; Plank and Hirsch, 2007). Initially, C<sub>3</sub>S and C-S-H have a negative surface charge.

Their surface can be covered with calcium ions, which changes the polarity to positive zeta potential values and makes them accessible for anionic SP adsorption (Mollah et al., 2000; Sakai et al., 2003; Zingg et al., 2008). Furthermore, the zeta potential of cement is reduced slightly by the adsorption of SPs (Flatt and Schober, 2012).

PCEs have several side chains attached to their backbones. These side chains cause steric hindrance, which is the main mechanism for improving flowability (Lei et al., 2022a). Raw smectite can swell (Jasmund et al., 1993), which increases its d-spacing in the c-axis direction and, more specifically, its interlayer spacing (Zhang and Low, 1989). Borralleras et al. (2019) showed that SP side chains can intercalate into the interlayer of raw smectite. This increases their d-spacing, depending on the SP content. The intercalation of SP side chains reduces the effectiveness of SPs (Lei et al., 2022b).

## 1.3. Interparticle forces

There are two main forces in a liquid-clay dispersion, one attractive and one repulsive force. The model to describe these forces is called Derjaguin–Landau–Verwey–Overbeek-theory (DLVO) (Derjaguin, 1941; Egan, 1975; Jasmund et al., 1993; Lagaly et al., 1997; Verwey, 1947). The DLVO-theory basically consists of three sections going from the particle core outwards to the undisturbed suspension: surface charge, Stern layer, and the diffuse layer. Solids in liquids usually have a charged surface. This charged surface creates a layer of counter-ions on top of the surface in an ordered manner, the so-called Stern layer which can be measured as the zeta potential. Going further away from the particle into the solution, there is a diffuse layer with co-ions. The co-ions have the same charge as the surface. This diffuse layer reaches into the undisturbed section of the solution. If two particles are getting closer together, their diffuse layers overlap. This causes a surplus of ions in their diffuse layer, resulting in an osmotic repulsive force depending on the particle radius ( $a$ ), the particle distance ( $h$ ), and the ionic strength ( $I$ ) in addition to the Stern potential ( $\Psi_s$ ). Lowke (2013) simplified the repulsive osmotic forces ( $F_{ed}$ ) for cementitious systems to:

$$F_{ed} = 4.47 \cdot 10^{-15} \cdot a^2 \cdot \Psi_s^2 \cdot \exp^{-1.04 \cdot 10^{-8} \cdot h \cdot \sqrt{I}} \quad (1)$$

$$I = 0.5 \cdot \sum c_i \cdot z_i^2 \quad (2)$$

$a$  = particle radius [m],  $h$  = particle distance [m],  $\Psi_s$  = Stern potential  $\approx$  zeta potential [mV],  $c_i$  = molar concentration [mmol/l] and  $z_i$  = charge

Van der Waals forces are interparticle attraction forces. They depend on the distance between particles and lose their importance at distances of 10 nm and higher (Jasmund et al., 1993). The van der Waals forces ( $F_{vdw}$ ) for low particle distances are simplified by Lowke (2013); (Flatt, 2004) to:

$$F_{vdw} \cong -A_s \cdot f_r(h_v) \cdot \frac{\bar{a}}{12h_v^2} \quad (3)$$

$A_s$  = Hamaker constant,  $f_r$  = retarder function,  $\bar{a}$  = particle radius [m],  $h_v$  = particle distance [m]

Even though many researchers have analyzed CCs, the rheological influence of CCs in cementitious systems is still a challenging aspect for the use as SCM, and many questions remain unanswered. Can smectitic clays swell after calcination and intercalate SP side chains? How do ions in pore solution, SPs, and CC surfaces interact and consequently affect rheological behavior when CCs is used as SCM? These questions are addressed with the use of four illitic and smectitic CCs analyzed in different pore solutions with XRD, infrared spectroscopy, rheometer, and electroacoustic measurements. The study provides a deeper understanding of the impact on rheological properties of CCs used as SCMs in cementitious systems.

## 2. Materials and methods

### 2.1. Material characterization

#### 2.1.1. Calcined clays

Four different CCs were used. Four raw clays from different local German providers were used. IllE is an illite dominated clay originally named “Ton E” from Sibelco Deutschland GmbH. IllA is also an illite dominated clay originally named “Arginotec Ton GI” from Hermann Nottenkämper GmbH & Co. KG. Smk is a smectite dominated clay originally named “Westerwald Bentonit” from Stephan Schmidt KG. SmI is a mixture of smectitic and illitic clay minerals originally named “Argarton” from Kärlicher Ton und Schamottewerke Mannheim & Co. KG. In the following a preceding “c” represents a calcined clay and a prefixed “r” represents a raw clay (e.g. cSmk and rIllE). Calcination temperature was chosen on basis of thermogravimetric measurement (Figure A1; appendix and supplementary data can be found online). All CCs were calcined for 2 h at 840°C in shuttle kilns. Subsequently, they were ground in tumbling mills with aluminum oxide cladding and grinding media. Resulting particle size distribution is displayed in Figure A2. Calcination and grinding were conducted by Helmut Kreutz Mahlwerke GmbH.

Mineralogy was determined on raw clays via XRD using a Panalytical Empyrean diffractometer at 40 kV and 40 mA with Cu K $\alpha$  radiation and a PIXcel<sup>1D</sup> linear detector. The diffractograms were taken from 4 to 70° 2 $\theta$  using BraggBrentano<sup>HD</sup> monochromator on samples after sideload preparation. The measurements were analyzed with Profex-BGMN (Doebelin and Kleeberg, 2015) using Rietveld refinement (Rietveld, 1967; Rietveld, 1969) with 30 m% ZnO as internal standard. Clay mineral identification was performed on oriented mounts of the < 2  $\mu$ m fraction in air-dried (AD) condition, after ethylene glycol (EG) solvation, and after heat treatment at 550 °C (550) using a nickel K $\alpha$ -filter and a variable divergence slit, which kept the irradiated length constant at 15 mm instead of the monochromator. Detailed information about the disaggregation, particle size separation, and preparation by the glass slide method (Moore and Reynolds, 1997) is given in (Maier et al., 2021a). The mineralogy of raw clays is displayed in Table 1.

The chemical analysis of the raw clays was carried out using ICP-OES (Varian 720 ES, Agilent Technologies) after a melt fusion with lithium metaborate as a fusing agent. The exact procedure is described in (Scherb et al., 2020). The measurements and evaluation were performed according to (DIN EN ISO 11885, 2009). The chemical composition of the raw clays is displayed in Table 2. Several physical parameters of CCs are displayed in Table 3. The type of smectite in rSmk and rSmI was evaluated based on mineralogy and chemical composition. rSmk contains an iron-rich montmorillonite. For rSmI, the high illite / mica content makes classification via chemical composition less certain, but smectite is most likely also montmorillonite.

For all measurements, clay sample preparation was the same. Raw clays were dried at 60°C for 6 d, CCs were dried at 105°C for 2 h. Afterwards, samples were stored for cooldown in a desiccator.

#### 2.1.2. Superplasticizer (SP)

A PCE was synthesized via copolymerization of polyethylene glycol methyl ether (often referred to as HPEG) as sidechain and acrylic acid as backbone monomer. Side chain length in molecular units of ethylene oxide was  $n_{eo}=52$ . The molar ratio of the backbone monomer (a) to side

**Table 2**

Chemical composition and loss on ignition (LoI) of raw clays.

| m%                             | rIllA | rIllE | rSmk | rSmI |
|--------------------------------|-------|-------|------|------|
| SiO <sub>2</sub>               | 44.5  | 55.4  | 56.3 | 49.8 |
| Al <sub>2</sub> O <sub>3</sub> | 17.9  | 17.0  | 15.3 | 16.0 |
| Fe <sub>2</sub> O <sub>3</sub> | 6.3   | 8.3   | 7.7  | 11.2 |
| CaO                            | 7.0   | 0.7   | 2.2  | 0.9  |
| MgO                            | 2.8   | 2.8   | 1.6  | 2.1  |
| Na <sub>2</sub> O              | 0.7   | 0.4   | 1.0  | 0.5  |
| K <sub>2</sub> O               | 5.1   | 5.2   | 1.2  | 2.9  |
| TiO <sub>2</sub>               | 0.7   | 0.8   | 1.7  | 1.0  |
| SO <sub>3</sub>                | 0.1   | 0.2   | 0.1  | 0.5  |
| LoI                            | 15.0  | 9.3   | 13.0 | 15.1 |

chain polymer (b) was 6. SP was named 52HPEG6. The SP characteristics are displayed in Table 4. SP was always added by weight of solid content (%<sub>bws</sub>). The structural formula is consistent with HPEG PCE in (Schmid and Plank, 2021). The SP was synthesized and characterized by joint research partner, Professorship for Construction Chemicals (Prof. Plank), Technical University of Munich.

#### 2.1.3. Model solutions

Four different model solutions were used. Deionized water (DIW), supersaturated portlandite solution (CHS), synthetic cement pore solution (SCPS) and 0.12 M KOH solution (KOHs). The corresponding composition is given in Table 5. The SCPS is a solution that imitates the pore solution of an ordinary Portland cement in the first two hours, regarding its pH value and its ion concentration (Kelzenberg et al., 1998; Schmid and Plank, 2021). It was prepared according to Habbaba and Plank (2012).

## 2.2. Methods

### 2.2.1. Rheometry

Rotational rheometry was used to determine dynamic yield stress and viscosity. First, a sample of 600 g solid content was weighed in. Then the solid material was poured onto the liquid and mixed according to DIN EN 196-3 (2017). About 4 min after liquid addition, the sample was poured into the rheometer Viskomat NT (Schleibinger) using the cement paste paddle. All materials were stored at 25°C prior to the experiment and temperature was kept at 25°C during measurement. The rheometric measurement started at 10 min after liquid addition and ended after 25.5 min. The measurement program is displayed in Figure A3. The yield stress and plastic viscosity were calculated using the Bingham model (Barnes and Walters, 1985; Hackley and Ferraris, 2001). The data point used was the average of the last 10 s of the steps 100-20 rpm, if an equilibrium was achieved. To exclude any time-dependent material behavior, equilibrium was considered when data had a variation coefficient < 1% and a slope inclination <  $\Delta 0,05$  Nmm/s, otherwise, that data point was excluded. The rheological parameters may not be the true parameters of the material since they also depend on the rheometer itself. Therefore, the apparent yield stress is reported in N-mm and the apparent plastic viscosity in N-mm-min (N-mm/rpm), rather than in the physical units of true yield stress and viscosity. Thus, they should only be used for comparisons within the data set. Any yield stress mentioned in this research is referring to dynamic yield stress.

**Table 1**

Mineralogy of raw clays, minor constituents of less than 5 m% are summed up and summarized in the last column. Minor constituents can be seen in Table SM1.

| [m%]  | kaolinite | illite / mica | smectite | feldspar | carbonates | quartz | <5 m% |
|-------|-----------|---------------|----------|----------|------------|--------|-------|
| rIllE | 10        | 74            |          |          |            | 11     | 5     |
| rIllA | 7         | 72            |          | 9        | 9          |        | 3     |
| rSmk  | 7         | 4             | 54       | 13       |            | 17     | 5     |
| rSmI  | 11        | 33            | 33       |          |            | 15     | 8     |

**Table 3**

Physical parameters of calcined clays (CCs).

| Parameter                   | Test method                  |                      | cIII E | cIII A | cSmk | cSmI |
|-----------------------------|------------------------------|----------------------|--------|--------|------|------|
| particle density            | (DIN EN ISO 17892-3, 2015)   | [g/cm <sup>3</sup> ] | 2.76   | 2.72   | 2.72 | 2.82 |
| BET specific surface area   | (DIN ISO 9277, 2003)         | [m <sup>2</sup> /g]  | 71     | 67     | 38   | 51   |
| particle size distribution  | (ISO 13320, 2020)            | d10                  | 2.8    | 2.5    | 2.4  | 2.6  |
|                             |                              | d50                  | 15.8   | 15.8   | 15.8 | 15.6 |
|                             |                              | d90                  | 49.6   | 60.7   | 56.3 | 60.5 |
| water demand                | (Puntke, 2002)               | [m%]                 | 53.4   | 55.6   | 45.0 | 50.6 |
| cation exchange capacity    | (Steudel and Emmerich, 2013) | [cmol(+)/kg]         | 11     | 12     | 7    | 7    |
| R <sup>3</sup> evolved heat | (ASTM C1897 - 20, 2020)      | 1 d                  | 183    | 167    | 128  | 163  |
|                             |                              | 7 d                  | 282    | 272    | 400  | 308  |

**Table 4**

Superplasticizer (SP) characteristics including molecular weights  $M_n$  and  $M_w$  as well as the polydispersity index (PDI). Detailed information on methodology for superplasticizer (SP) characterization can be found in Schmid and Plank (2021).

| PCE samples | $\alpha/b$ | side chain      | $M_w$   | $M_n$   | PDI           | Conversion rate of macromonomer [%] | Measured anionic charge amount [ $\mu\text{eq/g}$ ] |
|-------------|------------|-----------------|---------|---------|---------------|-------------------------------------|-----------------------------------------------------|
|             | [-]        | [ $\text{EO}$ ] | [g/mol] | [g/mol] | [ $M_w/M_n$ ] |                                     |                                                     |
| 52HPEG6     | 6          | 52              | 14,940  | 10,550  | 1.4           | 93.4                                | 2146                                                |

**Table 5**

Used model solutions with according constituents, calculated pH value and molar concentrations.

|      | KOH   | $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ | $\text{Na}_2\text{SO}_4$ | $\text{K}_2\text{SO}_4$ | $\text{Ca}(\text{OH})_2$ | pH   | $\text{Ca}^{2+}$ | $\text{K}^+$ | $\text{SO}_4^{2-}$ | $\text{Na}^+$ | $\text{OH}^-$ |
|------|-------|-------------------------------------------|--------------------------|-------------------------|--------------------------|------|------------------|--------------|--------------------|---------------|---------------|
|      | [g/l] | [g/l]                                     | [g/l]                    | [g/l]                   | [g/l]                    | [-]  | mol/l            | mol/l        | mol/l              | mol/l         | mol/l         |
| DIW  | -     | -                                         | -                        | -                       | -                        | 7.0  | -                | -            | -                  | -             | -             |
| KOHS | 7.120 | -                                         | -                        | -                       | -                        | 13.1 | -                | 0.127        | -                  | -             | 0.127         |
| SCPS | 7.120 | 1.720                                     | 6.959                    | 4.257                   | -                        | 13.1 | 0.010            | 0.176        | 0.083              | 0.098         | 0.127         |
| CHS  | -     | -                                         | -                        | -                       | 2.000                    | 12.7 | 0.027            | -            | -                  | -             | 0.054         |

### 2.2.2. Electroacoustic measurements

To determine adsorption mechanisms on CC surfaces zeta potential measurements were conducted by electroacoustic measurements with a DT-310 spectrometer (Dispersion Technology Instruments). For general surface charge measurements in model solutions, a sample of 80 g CCs and 240 g of model solution were weighted in resulting in a liquid/solid ratio (w/s) of 3.0. The sample was stirred at 200 rpm, and the measurement started 4 min after liquid addition.

In addition to the previous parameters for calcium and sulfate titration experiments, the pH value was adjusted via a 1 M KOH solution. The pH value was adjusted to the highest initial pH value of the four CCs (cSmk, pH 12.0). The pH value was kept constant with further titration of 1 M KOH solution throughout the measurement. To determine calcium adsorption 1 M  $\text{CaCl}_2$  solution was added stepwise with an automatic titration system. For sulfate adsorption measurements, an initial concentration of 20 mg<sub>calcium</sub>/g<sub>solid</sub> via 1 M  $\text{CaCl}_2$  was added to CHS. Then, a 1 M  $\text{Na}_2\text{SO}_4$  solution was added stepwise via an automatic titration system. Measurement procedures were based on Maier et al. (2022) and Schmid and Plank (2021).

A w/s ratio 0.9 was used for measurements, simultaneously investigating the influence of calcium and SP addition on zeta potential and rheological behavior. The liquid used was KOHS. Calcium was added via solid  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and SP was added as liquid with a solid content of 38.77 m%. This changed w/s ratio by less than  $\Delta 0.05$ . The pH values were not adjusted. The mixing protocol was identical to the previous rheological measurements. After mixing, the sample was split for the rheometer and the zeta potential tests. The first addition of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  was equivalent to 0.36 mg<sub>calcium</sub>/g<sub>solid</sub>, the second addition was equivalent to 20 mg<sub>calcium</sub>/g<sub>solid</sub>. Then SPs were added in four steps with 0.5%<sub>bwos</sub> each step.

### 2.2.3. X-ray diffraction

Crystalline hydration products were investigated at early times (ettringite, portlandite) via in situ XRD measurements with a

PANalytical Empyrean in a theta/theta Bragg-Brentano configuration with  $\text{CuK}\alpha$  (1.54 Å) radiation. The set up consisted of a primary Bragg-BrentanoHD monochromator, 0.04 rad soller, slits and a PIXcel1D linear detector. The investigated systems were CCs, each with SCPS at a w/s ratio of 0.6. The samples were stirred manually and prepared in corresponding crucibles using a flat stage and covered with 12  $\mu\text{m}$  thick Kapton foil. The measurements started 4 min after liquid addition and were conducted in a continuous scan mode with a step size of 0.013 at a counting time of 25.5 s per step at 40 kV and 40 mA. In the first 2 h a scan range from 7.5 to 19° 2 $\theta$  was chosen to achieve a high time resolution (5 min per scan). From 2-48 h it was 7.5 to 40° 2 $\theta$ . The evaluation of the measurements was done with HighScore Plus 4.8.

To measure swelling and intercalation, the previous set up was adjusted to the scan range from 3 to 30° 2 $\theta$  and a w/s ratio of 0.5. The test series consisted of the dry rSmk and cSmk, each with DIW and with DIW and 8%<sub>bwos</sub> SP addition. Measurement started 5 min after liquid addition with a duration of 2 h. The preparation height error was corrected using the quartz content of the clay samples. The raw data were then smoothed with an FFT-filter (Origin 2023), and the positions ( $d$ -values) of the maximum of the (001) reflection of the smectite samples were determined.

### 2.2.4. Gravimetric water absorption

The Enslin-Neff method (DIN 18132, 2012) was used to determine the water absorption capacity of raw clays and CCs samples. To stay within in the available water absorption measurement range of 2.0 ml, the weigh in was reduced to 0.2 g. After the samples were placed on the filter plate, they absorbed water over time via capillary uptake, which marks the beginning of the experiment. The absorbed water was read from the measurement scale. Parallel evaporation was measured and subtracted from the readings.

### 2.2.5. Infrared spectroscopy

Infrared spectroscopy (FTIR, Nicolet iS10, ThermoFisher Scientific)

was used to determine SP adsorption on CCs in different aqueous solutions via centrifuging (Table 6). The aqueous solutions were prepared using KOHS, 52HPEG6,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . Crystal water and liquid SP content were considered in DIW addition. w/s ratio was 1.5.

Sample preparation was done according to Figure 1. CCs were poured on top of the aqueous solution and stirred.  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  was always added after CC. The sample was homogenized for 10 min at 400 rpm and then poured into test tubes. Test tubes were centrifuged for 10 min at 4500 rpm. About 25 ml of liquid was pipetted, weighed and dried for 6 d at 40°C. 2 ml of DIW was added to dried SPs and stirred for about 10 min until all solids were dissolved. Then 0.2 ml was used for FTIR measurements.

To determine SP content, the extinction of reference SP and DIW mixtures with fixed SP amounts was measured (Figure A4). With this data a linear fit was made combining extinction and SP content, which enabled the calculation of the SP content of the liquid. Since total SP content is known, the adsorbed SP content on the CCs was calculated via simple subtraction. To emphasize the signal of pore solution, the pore solution was dried, reliquified and rescaled to the original weight. The extinctions of the samples were between 0.0075 and 0.0250  $\text{cm}^{-1}$ . All SP extinctions were measured at a band at wavenumber  $\sim 1350 \text{ cm}^{-1}$ ; this corresponds to a carboxylate band ( $\text{COO}^-$ ). The more intense ether band (C-O-C) at 1083  $\text{cm}^{-1}$  overlaps with the sulfate band (S-O) at 1091  $\text{cm}^{-1}$  and therefore, could not be used for evaluation. Exemplary extinction patterns of SP and SP with CC and ion addition can be seen in Figure SM1. The evaluation of the data was carried out with Omnic 9.12.

### 3. Results and discussion

#### 3.1. Intercalation of superplasticizer side chains into smectite interlayers and swelling

To investigate intercalation of SPs into the smectite interlayer, the  $d$ -value of raw and calcined Smk in the presence of water and SP was observed (Table 7). The  $d$ -value increased for rSmk with the addition of DIW. This confirmed swelling of Smk due to water addition. It increased even further with SP. The increase in  $d$ -value with SP addition was attributed to SP side chain intercalation into the interlayers of rSmk (Borralleras et al., 2019; Ma et al., 2022; Ng and Plank, 2012). The  $d$ -value for cSmk exhibited noticeable difference for the dry or the wet state, with or without SP. The calcination of smectite eliminated its potential to swell as indicated by fundamental research (Emmerich et al., 2001) and thus, the possible intercalation of SP side chains.

Measurements for water absorption capacity also indicated, that after the calcination swelling of smectites was no longer possible. Water absorption of swelling clays takes time and is known to be high (Madsen and Müller-Vonmoos, 1989; Zhang and Low, 1989). As shown in Figure 2, rSmk needed up to 4 h to finish water absorption. After calcination, cSmk finished water absorption within 8 min while reducing the water absorption capacity to less than 50%. This was in line with the results of the water demand according to Puntke (Table 3) of the four CCs investigated, which were all approximately around 50 wt.% and cSmk even had the lowest water demand. This indicated that cSmk cannot swell anymore, and consequently, SP side chains cannot intercalate into the interlayers of a calcined smectite.

**Table 6**

Aqueous solutions for FTIR using potassium hydroxide solution (KOHS), superplasticizer (SP),  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .

|   | aqueous solution | KOH<br>[g/l] | 52HPEG6<br>[% <sub>bwos</sub> ] | calcium<br>[mg/g <sub>solid</sub> ] | sulfate<br>[mg/g <sub>solid</sub> ] |
|---|------------------|--------------|---------------------------------|-------------------------------------|-------------------------------------|
| a | w/o              | 7.12         | 4                               | -                                   | -                                   |
| b | w/calcium        | 7.12         | 4                               | 20                                  | -                                   |
| c | w/sulfate        | 7.12         | 4                               | 20                                  | 20                                  |

SP side chain intercalation and high water absorption capacity were a concern regarding raw smectites (Lei et al., 2022b). These concerns could be resolved for calcined smectites and promote the use of calcined smectites as SCM in cement.

#### 3.2. Hydrate phase formation of calcined clay in synthetic cement pore solution

Figure 3 shows the XRD measurements of all four CCs on dry powder and SCPS-paste immediately after (0 h) and 2 h after liquid addition. None of the CCs formed any detectable crystalline hydrate phases. This holds true for a further measurement until 48 h, and measurements with increased calcium content via  $\text{CaCl}_2$  addition (21  $\text{mg}_{\text{calcium}}/\text{g}_{\text{solid}}$ ). This differs from the results in the literature (Maier et al., 2023; Scherb et al., 2021), who showed that CCs can form hydrate phases on their own during early hydration. Nevertheless, this is not contradictory, as portlandite is not available as a reaction partner in the present investigations. The ion concentration in the SCPS may not be high enough for the independent formation of hydrate phases. In conclusion, ettringite formation was excluded as a causal influence on rheological properties for CCs in this study and its known influence on the workability of cementitious systems (Jakob et al., 2019; Rößler et al., 2008; Zingg et al., 2008).

The reflections in the diffractograms at approximately  $8.8^\circ 2\theta$  were attributed to the phyllosilicates illite, muscovite, and smectite, which retained parts of their crystalline structure after calcination despite dehydroxylation. In the case of smectite, calcination led to a collapse of the swelling interlayer and thus, to a broad reflection in the diffractogram in the area of the (001) and (002) reflections of illite and muscovite, respectively.

#### 3.3. Calcined clay adsorption mechanism of calcium and sulfate

Figure 4a shows zeta potential measurements with the titration of  $\text{CaCl}_2$ . The initial zeta potential of all CCs was negative in the range of -5 to -20 mV. This was similar to previous findings (Maier et al., 2022; Schmid and Plank, 2021; Sposito et al., 2020). The initial zeta potential depended on the individual CC. Even CCs with similar mineralogy, cille and cilla, display different zeta potentials.

With the addition of  $\text{CaCl}_2$ , all CCs became positive with a jump from  $\sim -6$  mV above the isoelectric point to about 5 mV. This general behavior has already been reported by (Li et al., 2021; Lowke and Gehlen, 2015). The divalent charge of calcium ions was responsible for the relatively fast (Frey and Lagaly, 1979) change in polarity of the charge in zeta potential ( $\sim 6 \text{ mg}_{\text{calcium}}/\text{g}_{\text{solid}}$ ) and strong interaction in cementitious systems in general (Lowke, 2013). Once the surface charge of the CCs became positive, it slowly converged towards a plateau of around 7 to 8 mV with a total addition of about 20  $\text{mg}_{\text{calcium}}/\text{g}_{\text{solid}}$ . The difference in zeta potential from before titration until the plateau could be seen as a measure of the calcium uptake by a CC (Schmid and Plank, 2021).

Jansen et al. (2018) showed with their complete mass balance approach that the adsorption of calcium ions on surfaces in cementitious systems appears initially. Their initial calcium adsorption was calculated to be about 23  $\text{mg}_{\text{calcium}}/\text{g}_{\text{solid}}$ . It could therefore be assumed that 20  $\text{mg}_{\text{calcium}}/\text{g}_{\text{solid}}$  is a realistic amount available for adsorption in a cementitious system during early hydration. Due to the presence of other constituents in cement that adsorb calcium, and depending on the cement replacement ratio with CCs, there may not be enough calcium ions available for a full surface coverage. Since CCs exhibited charge reversal at 8  $\text{mg}_{\text{calcium}}/\text{g}_{\text{solid}}$  or less, positively charged CC surfaces are likely to occur. It could be concluded that zeta potential values of CCs in a cementitious system will be much higher than in an isolated system without cations.

Figure 4b displays the sulfate adsorption after an initial calcium addition of 20  $\text{mg}_{\text{calcium}}/\text{g}_{\text{solid}}$ . All CCs behave similarly. The zeta potential declines and levels off at around 20  $\text{mg}_{\text{sulfate}}/\text{g}_{\text{solid}}$ . This was

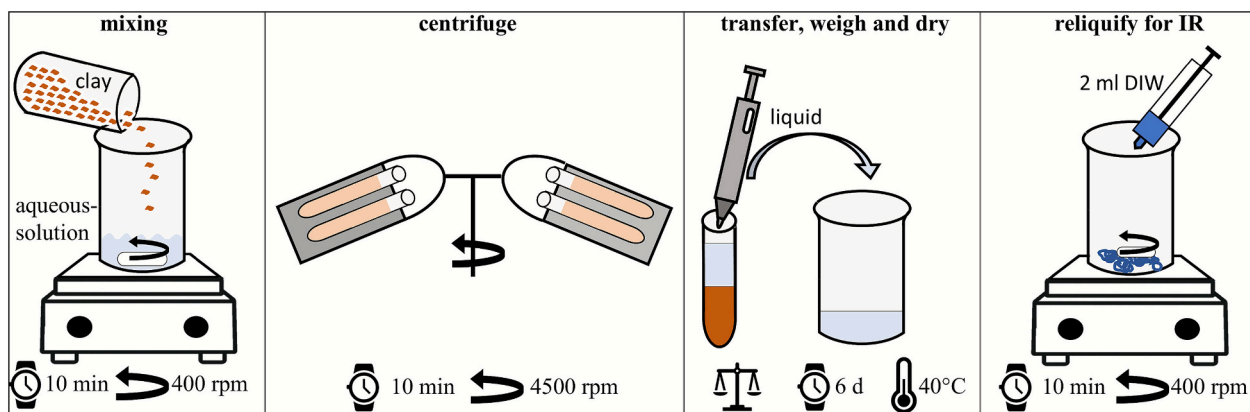


Fig. 1. Sample preparation for superplasticizer (SP) adsorption measurements in FTIR. Mixing was done with a magnetic stirrer.

Table 7

*d*-value (001) for Smk in raw and calcined state measured dry, in water and in water with superplasticizer (SP).

| Sample               | <i>d</i> -value (001)<br>raw<br>[Å] | <i>d</i> -value (001)<br>calcined<br>[Å] |
|----------------------|-------------------------------------|------------------------------------------|
| Smk, (dried at 60°C) | 13.15                               | 10.07                                    |
| Smk with DIW         | 20.05                               | 10.12                                    |
| Smk with DIW and SP  | 22.30                               | 10.15                                    |

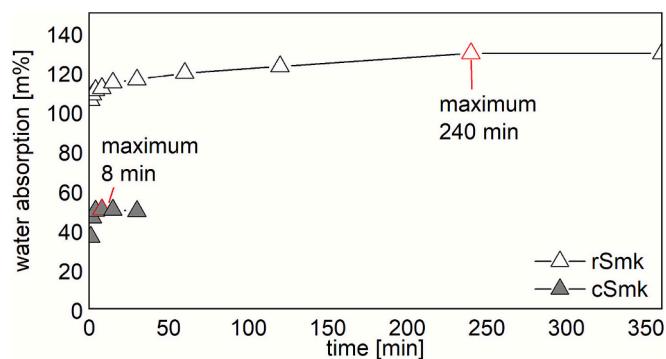


Fig. 2. Water absorption capacity of raw and calcined smectite.

congruent with findings of Maier et al. (2022). According to Stern-layer-theory such an effect was expected, since most of the co-ions should be in the diffuse layer, which is generally not measured with zeta potential (Jasmund et al., 1993; Lowke and Gehlen, 2015). The higher the ionic concentration is, the more ions will move from the diffuse layer towards the Stern layer (Eagland, 1975; Lowke, 2013) and may be measured within zeta potential measurements. This can be seen in the continuous decline in zeta potential throughout the sulfate titration.

### 3.4. Rheological parameters of calcined clay in deionized water and synthetic cement pore solution

Rotational rheometry was conducted with CCs in DIW and SCPS (Table 5). The yield stress increased with the increase of ion concentration in solution (Figure 5, top), while viscosity did not change significantly (bottom).

For all CCs an increase in yield stress in SCPS compared to DIW was seen of about 10 Nmm, depending on the CC, it ranged from 25 to 460%. cIIIE in SCPS even became unmeasurable in the rheometer. A rise of the w/s ratio by 0.15 up to 0.9 did not change that. CCs yield stress was highly influenced by the SCPS. This held true especially for cIIIE. In

Chapter 3.2, possible phase hydrate formations, especially ettringite, were ruled out as a reason for changes in rheological properties. Some yield stress values in this research were below 0, which is physically impossible. This may have been due to the Bingham model extrapolating from 20 rpm to 0 rpm, as the material had comparably high viscosity and most CCs showed slightly dilatant flow behavior.

The observed changes in yield stress could be due to a change in the balance of the attractive and repulsive interparticle forces. The change in rheological behavior due to different ion concentrations was described by others (Jasmund et al., 1993; Real et al., 2025) as coagulation. A reduction in osmotic repulsion allows particles to move closer together. Since Van der Waals forces increase significantly at shorter distances (equation 3), a critical coagulation point can be reached. Beyond this point, due to a larger attractive force, the system becomes unstable, leading to particle aggregation. This results in a coagulated, gel-like texture.

The repulsive osmotic forces depend on the particle radius, particle distance, zeta potential, and ionic strength according to equation 1 (Lowke, 2013). Table 8 provides the zeta potential of the CCs in the solutions DIW and SCPS. Additionally, the zeta potential values and ratios with KOHS are listed, which will be addressed in Chapter 3.5. Since zeta potential was squared for calculating the osmotic repulsive force, the squared ratio of SCPS to DIW is also displayed. All CCs' zeta potential increased (to more positive values) from DIW to SCPS, which resulted in a reduction of osmotic repulsive force in SCPS to about 10 to 15% compared to the value in DIW. The ionic strength is determined by the charge and concentration of ions in the solution and therefore, increased uniformly for all CCs in SCPS by 333 mmol/l (Table 5; equation 2). According to equation 1, an increase in ionic strength reduces the osmotic repulsive force. Since the ionic strength in CCs DIW systems was not measured an exact value cannot be calculated. The particle radius was not influenced by the type of solution and therefore did not lead to a change in the repulsive force.

Different ion concentration does not alter the intrinsic Van der Waals parameters (Jasmund et al., 1993). However, as described above, the reduction in osmotic repulsion decreases interparticle spacing. Because the Van der Waals force scales inversely with the square of this interparticle spacing, the effective attraction becomes substantially stronger. This may have led to a coagulation of cIIIE while the other CCs did not reach the critical coagulation point. Similar behavior has been reported for metakaolin as well (Real et al., 2025). Their reduction in osmotic repulsive forces could explain their increased yield stress (Demeusy et al., 2023).

This change in repulsive forces could not be the sole explanation. Otherwise, cIIIE should not have been the sole CC displaying very strong coagulation effects. Even though materials have similar particle size distributions, that of cIIIE is slightly more monomodal than those of the other CCs (Figure A2). This can have an effect on the packing density,

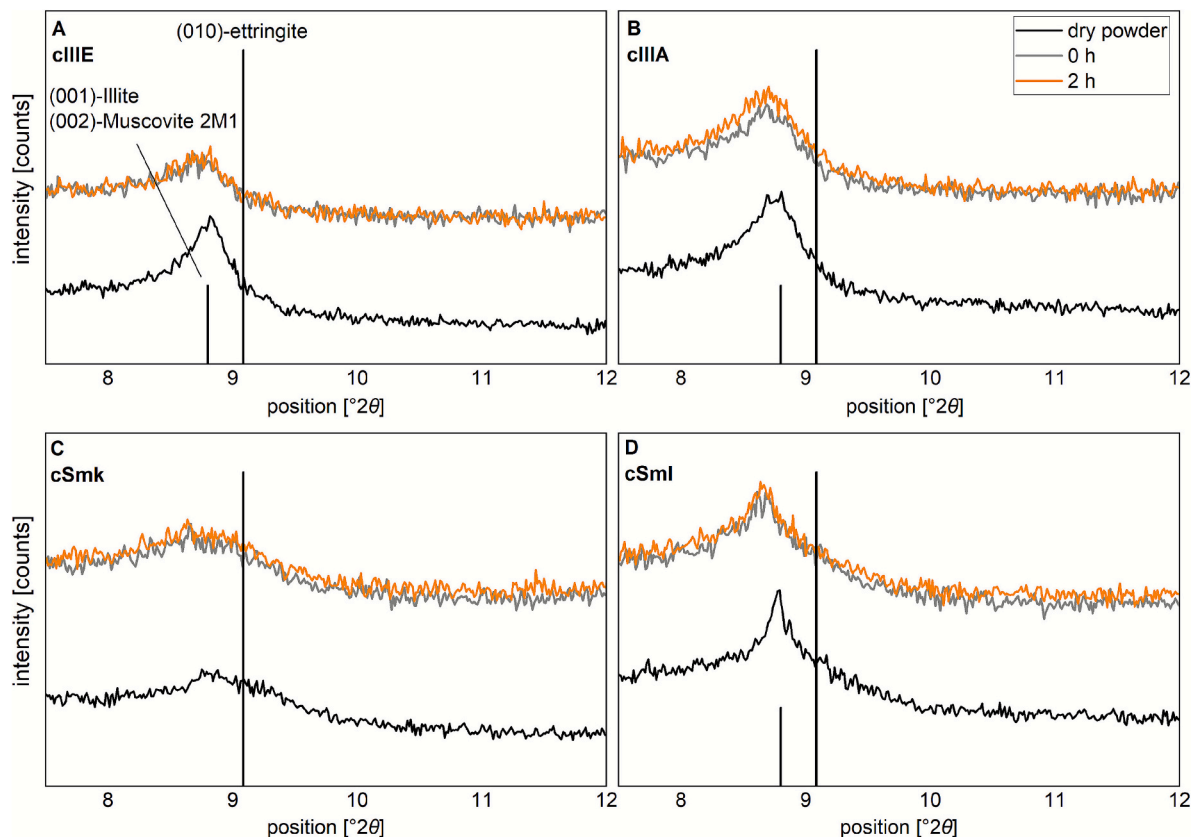


**Fig. 3.** X-Ray diffractogram for analysis of phase development. (010)-reflection of ettringite at  $9.086^{\circ}2\theta$  is marked by lines according to (Goetz-Neunhoeffer and Neubauer, 2005); (001) illite (Drits et al., 2010) and (002) muscovite 2M1 (Catti et al., 1994) reflections marked at approximately  $8.87^{\circ}2\theta$ .

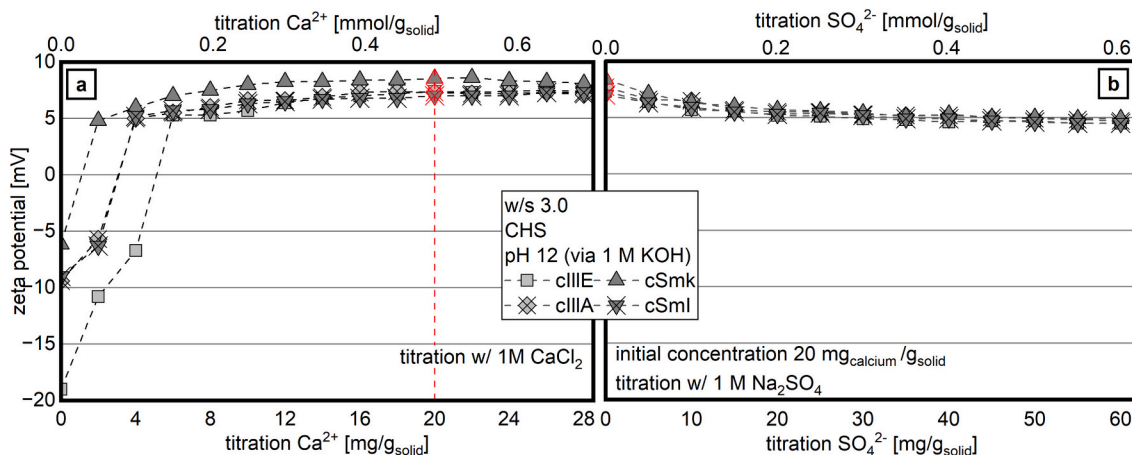


**Fig. 4.** Zeta potential measurements in calcium hydroxide solution (CHS) for (a) calcium adsorption via the addition of 1 M  $\text{CaCl}_2$  and (b) sulfate adsorption via the addition of 1 M  $\text{Na}_2\text{SO}_4$ . All suspensions' pH values were titrated from initial pH values (cIIIE 11.0; cIIIA 11.8; cSmk 12.0; cSmI 10.9) with 1 M KOH to pH 12.0 and kept constant during the whole measurement.

particle distance and therefore, interparticle forces (Flatt and Bowen, 2006). The present work cannot definitively determine this factor. This led to the conclusion that repulsive forces were a major, but not the only factor. Other parameters needed to be considered, such as inhomogeneous surface charge distribution (Flatt, 2004), particle size of the clay minerals, as well as mineralogical composition, especially content and type of clay minerals.

The reduction in repulsive forces due to the increase in zeta potential and ionic strength did not significantly affect viscosity (Figure 5, bottom). Even though, in general, a reduction in repulsive forces is known

to increase viscosity (Lagaly et al., 1997; Schramm, 2000), diffuse layers obstruct translatory and rotary movement of particles. Increased ionic strength due to higher ion content reduces the size of the diffuse layer and therefore, promotes movement, which can be seen in a reduced viscosity.

There could be several reasons why viscosity remained constant. According to (Nash, 1958; Touati et al., 2010) there is a span of salt concentration with no or no significant impact on viscosity. Viscosity only changes when there is just the right salt-to-clay ratio available to enable edge-face contacts. Another possibility was that the initial

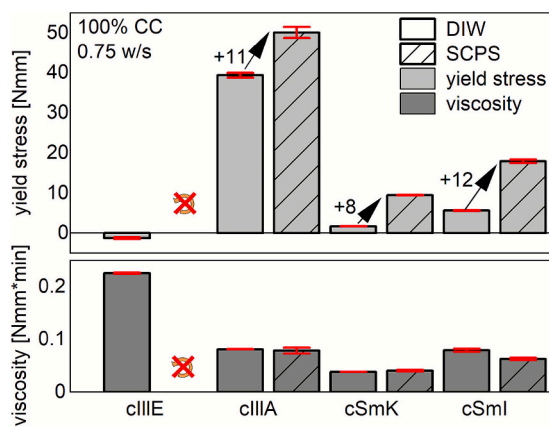


**Fig. 5.** Yield stress (top) and viscosity (bottom) measured in deionized water (DIW) and synthetic cement pore solution (SCPS) by rotational rheometry. The w/s ratio was 0.75. Arrows indicate absolute change in yield stress. The measurement of cIIIE in synthetic cement pore solution (SCPS) was not feasible due to wall slippage. Rheometer flowcharts can be found in Figure SM2-3.

**Table 8**

Zeta potential of calcined clays (CCs) in different solutions with a w/s 3.0. The quadratic zeta potential is displayed as a ratio in between synthetic cement pore solution (SCPS) and potassium hydroxide solution (KOHs) compared to deionized water (DIW).

|                                                           |      | cIIIE | cIIIA | cSmK  | cSmI  |
|-----------------------------------------------------------|------|-------|-------|-------|-------|
| DIW                                                       | [mV] | -34.9 | -17.7 | -18.3 | -19.6 |
| SCPS                                                      | [mV] | -11.2 | -7.0  | 6.2   | 6.2   |
| KOHs                                                      | [mV] | -34.8 | -20.7 | -19.4 | -17.9 |
| Zeta potential in:<br>SCPS <sup>2</sup> /DIW <sup>2</sup> | [%]  | 10.9  | 15.6  | 11.5  | 10.3  |
| Zeta potential in:<br>KOHs <sup>2</sup> /DIW <sup>2</sup> | [%]  | 99.4  | 136.8 | 112.3 | 83.4  |

influence of ionic strength may have had a subordinate role on viscosity in the first place, and a decrease resulted subsequently in an insignificant impact. According to Lagaly et al. (1997) other responsible parameters for viscosity could be particle size and shape, and solid volume fraction (Robinson, 1949). Overall, the study cannot give a finite answer on the unchanged viscosity in different suspensions.

### 3.5. Effect of ion addition on surface charge and rheology

A better insight could be gained on the influence of ions in pore solution on the rheology and surface charge via combined electroacoustic and rheometer measurements with a stepwise ion and SP addition. First the initial data before ion addition in KOHS were compared to previous results in DIW, SCPS (Chapter 3.4), and CHS (Chapter 3.3).

The pH values (Figure 6-a) were initially at 10.5 or higher, but the yield stress was still close to 0 or very low, like the yield stress in DIW measurements (Figure 5) with much lower pH values (5.9 – 11.1). This confirmed results by Au and Leong (2013); (Au et al., 2014) showing that generally a higher pH value either reduces or does not influence the yield stress of raw clays. Thus, the rheological challenges of CCs in cementitious systems were not directly affected by the high pH values of cement. This explicitly excludes the well-known effect of pH on the zeta potential of CCs, and the subsequent influence of zeta potential on yield stress.

Yield stress (Figure 6-d) seemed highly influenced by changes in osmotic repulsive forces, as postulated previously in Chapter 3.4. Yield stress could not be compared directly to Figure 5, since an adjustment of w/s from 0.75 to 0.9 was made. This is why all CCs have a much-reduced

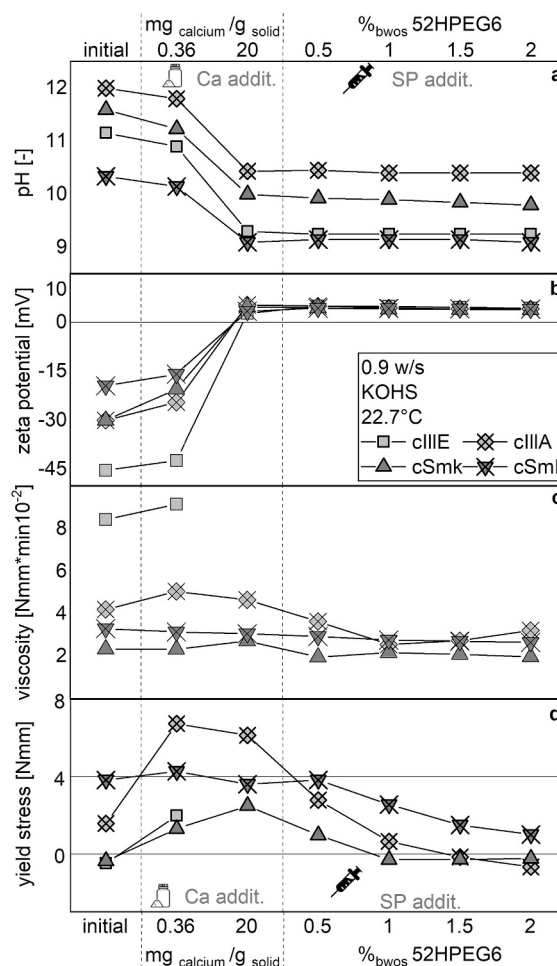


**Fig. 6.** Electroacoustic and rheometric measurements with two additions of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (0.36 and 20  $\text{mg}_{\text{calcium}}/\text{g}_{\text{solid}}$ ) and four additions of 52HPEG6 (0.5%<sub>bwos</sub> per step). The figure shows pH value (a), zeta potential (b), viscosity (c) and yield stress (d). The pH values were not adjusted and therefore, were different for all calcined clays (CCs) and changed throughout the measurement. The X-axis shows the discrete addition steps, not scaled by amount. According rheometer flowcharts can be found in Figure SM4-7.

yield stress, though the order of yield stress for cIIIA and cSmI in KOHS is not congruent with the order measured in DIW (Figure 5). Going from DIW to KOHS the zeta potential of cIIIA decreased by -3.0 mV and cSmI increased by +1.7 mV. This changed the osmotic repulsive force for cIIIA of +37% and for cSmI of -17% (Table 8), resulting in a delta of about 53% between the CCs. This explained the change of CCs order in yield stress and showed once more that the yield stress of CCs in aqueous solutions was highly influenced by zeta potential and subsequently by osmotic repulsive force.

Data in Figure 6-b and c confirm what was postulated in Chapter 3.3. The zeta potential and subsequently the reduction in repulsive forces had no significant influence on the viscosity. The zeta potential increased significantly with the addition of calcium, yet the viscosity remains the same. The SP addition reduced viscosity slightly, especially in the first and second addition steps. This effect has also been seen in cementitious systems with CCs (Sposito et al., 2022).

Zeta potential measurements in KOHS (Figure 6-b) behaved similarly to the measurements previously displayed in CHS (Figure 4). Generally, zeta potential values were lower, and cSmI and cSmK have changed order. That may have been due to their different initial pH value (cSmK = 11.6; cSmI = 10.3).

At high pH an increase in calcium content can lead to a precipitation of  $\text{Ca}(\text{OH})_2$ . The higher the content of calcium the lower the minimum

pH value needs to be. In a solid free solution at a calcium concentration of 0.554 mol/l (equivalent to 20mg<sub>Calcium</sub>/g<sub>solid</sub> at w/s 0.9), the required minimum pH value is 11.5. Solids affect precipitation in many ways such as nucleation surfaces and ion adsorption. Nevertheless, precipitation seems likely and possible for the systems analyzed here. A precipitation of Ca(OH)<sub>2</sub> results in a reduced pH value, which was observed after calcium addition (Figure 6-a). Attributing the drop in pH to solely Ca(OH)<sub>2</sub> would result for cIIIA in approximately 0.36 g/l, which is the equivalent of 0.0325 wt% Ca(OH)<sub>2</sub> per g CC. Ca(OH)<sub>2</sub> precipitation is likely, but the possible amount of precipitation seems negligible on parameters other than pH, due to its low gravimetric content.

Demeusy et al. (2023) described an increase in yield stress due to the addition of calcium ions to the solution. This general effect can be seen in Figure 6-d as well, but there seems to be no direct correlation between the amount of calcium addition and the yield stress increase. There seemed to be an influence on the yield stress up to a CC specific threshold, and then it showed no further significant effect.

Adding 0.36 mg<sub>calcium</sub>/g<sub>solid</sub> increased the yield stress for all CCs; cIIIA showed the highest increase by 6 Nmm. A further addition to a total content of 20 mg<sub>calcium</sub>/g<sub>solid</sub> had a negligible impact on cSmI and cIIIA, while cSmk exhibited an increase in yield stress. On the other hand, cIIIE thickened up and visually, a tremendous increase appeared in viscosity and/or yield stress. Due to occurrence of wall slippage, the rheometer could not obtain proper data. To obtain a reasonably homogeneous paste, the stirring speed used during the zeta-potential measurements had to be doubled. It seemed like cIIIE has surpassed its critical coagulation point and has become a more gel-like consistency. Such behavior is known from raw clays and high salt concentrations as described in Chapter 3.4 (Jasmund et al., 1993).

A closer look at the difference of zeta potential measured before (initial) and after calcium addition (20 mg<sub>calcium</sub>/g<sub>solid</sub>), revealed that the bigger the difference in zeta potential, the higher the yield stress increase due to calcium addition. cSmI had the lowest difference in zeta potential (22.9 mV), and its yield stress was basically not affected. cIIIE had the highest difference in zeta potential (48.0 mV), and its workability decreased tremendously, even exceeding the measurement boundaries of the rheometer. This effect was exaggerated considering the quadratic nature of the zeta potential on the osmotic repulsive force as described in Chapter 3.3. The osmotic repulsive force calculations did not match the yield stress behavior for the initial addition of 0.36 mg<sub>calcium</sub>/g<sub>solid</sub>. At low calcium contents, other factors must have played a more dominant role. This could have been due to different adsorption mechanisms at different calcium concentrations. Besides the regular adsorption of counter-ions on the surface of one CC particle (DLVO-theory), two CC particle surfaces could have shared one layer of counterions, the so-called central counter-ion plane (Jasmund et al., 1993; Kleijn and Oster, 1982). The central counter-ion plane adsorption of calcium ions could explain the exaggerated impact on yield stress at low zeta potential changes.

The addition of SP reversed the increase in yield stress due to calcium or reduced it even further, except for cIIIE. cIIIE still displayed wall slippage at 2%<sub>bwos</sub> SP addition. The yield stress-reducing effect of PCE-based SP in combination with CCs in cementitious systems was shown by others (Li et al., 2021; Sposito et al., 2022; Sposito et al., 2019; Stecher and Plank, 2020). The change in zeta potential after SP addition (~0.3 to 1.2 mV, Figure 6-b) confirmed that SPs adsorb on calcium-saturated CC surfaces (Flatt and Schober, 2012). This adsorption is also evident in systems using metakaolin (Derkani et al., 2022). Thus, results confirmed that anionic SPs adsorb on calcium-saturated CC surfaces and this effect improves the workability.

To summarize the main findings of this chapter: The pH value had no direct effect on the rheological behavior of the CCs. Calcium adsorption increased the yield stress of the CC. This was likely due to calcium's influence on zeta potential and subsequently, on the osmotic repulsive force (described in Chapter 3.4). Viscosity was not affected by calcium addition and change in zeta potential.

### 3.6. Superplasticizer adsorption capacity of calcined clay in different solutions

Figure 7 shows the amount of SPs adsorbed on the CC surfaces in KOHS + SP solution (a) and with the addition of calcium (b), and with the addition of calcium + sulfate (c). CCs can adsorb anionic superplasticizers directly onto their negatively charged surfaces, without the need for prior cation saturation (Figure 7-a). This may have been due to the inhomogeneous structure of clay, consisting of edges and faces. Even though the average surface charge of a CC was negative (Table 8), several authors (Frey and Lagaly, 1979; Jasmund et al., 1993) suggest that edge and face surfaces of raw clays can have different charge values. Sometimes they even have a different charge polarity (e.g. face negative and edge positive). There is no data available for CCs, though it is possible that similar variations in surface charge—observed in raw clays—also occur in CCs. Another origin for different charges could have been due to the substitution of octahedral positions by foreign ions with different valences. This could create local charge anomalies on CCs' base layers (Kaufhold, 2006; Kuligiewicz et al., 2015). Considering this and the data from Figure 7-a, anionic SPs may have adsorbed on positively charged edge or base sites, even though the CCs in total had a negative surface charge. This concept is illustrated for different edge charges in Figure 8-a.

Li et al. (2022) suggested, that SP adsorption in cementitious systems is only possible after calcium addition. Previous results showed that calcium adsorption increased the SP adsorption drastically, but SPs could adsorb on CC surfaces even without calcium in the solution. As discussed in Chapter 3.3, it remains unclear how much calcium will be available for adsorption on CCs in a cementitious system, and how much the SP demand will be affected.

With the addition of calcium, the total amount of SPs adsorbed increased drastically by more than 100% for all investigated CCs. A similar effect has been seen for metakaolin as well (Real et al., 2025). The previous zeta potential measurements (Figure 4-a), revealed that calcium ions adsorb on negative CC surfaces and led positive polarity. This effect enabled the anionic SPs to adsorb onto the positive charged Stern layer (Figure 7-b and Figure 8-b), which was confirmed by previous zeta potential measurements given in Figure 6. These findings are similar to results of other authors, including research on metakaolin (Derkani et al., 2022; Mollah et al., 2000; Real et al., 2025; Sakai et al., 2003; Zingg et al., 2008) regarding clinker phases and hydrate phases in cementitious systems, that initially displayed a negative surface charge and after adsorption of positive calcium ions, they were able to adsorb SPs.

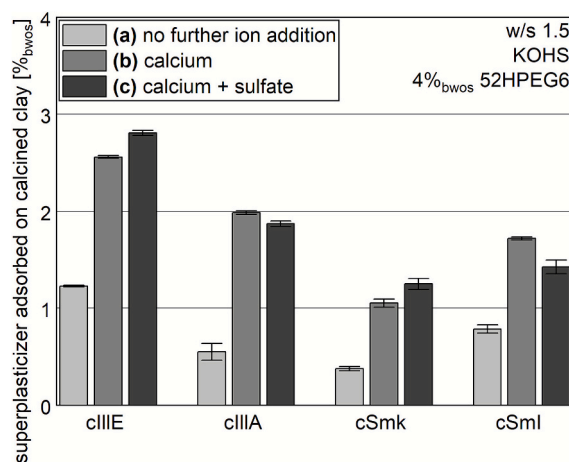


Fig. 7. Superplasticizer (SP) adsorption on calcined clay (CC) surfaces in different aqueous solutions. Ions were added via CaCl<sub>2</sub>·2H<sub>2</sub>O and Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O to an equivalent of 20 mg calcium or sulfate per g<sub>solid</sub>.

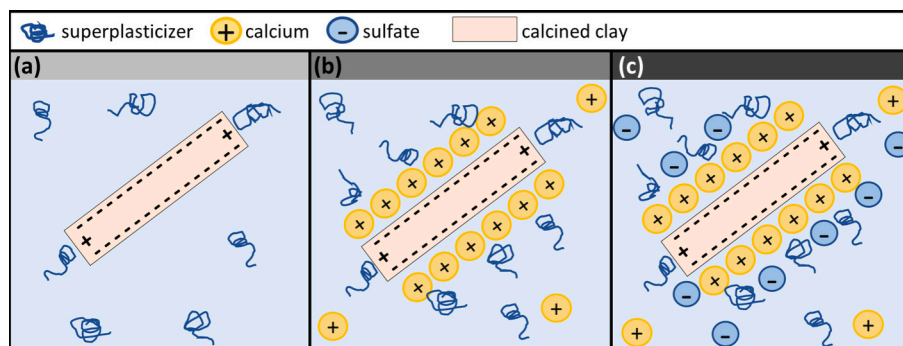


**Fig. 8.** Model superplasticizer (SP) adsorption on calcined clay (CC) surfaces depending on face or edge site. Aqueous solutions: (a) no further ion addition (b) calcium addition (c) calcium and sulfate addition

Clearly, the SP adsorption of calcined smectites was not extraordinarily high; it was even lower than that of illitic CCs. This indicated again that the use of fully dehydroxylated calcined smectite as SCM does not go along with the risk of intercalation of SPs and subsequent loss of fluidity as pointed out for raw smectites by Lei et al. (2022a, 2022b).

The SP adsorption in a system with calcium and sulfate showed only a minor change (Figure 7-c and Figure 8-c). For the CCs cIIIE and cSmk it was slightly higher, for cSmI and cIIIA it was somewhat lower. This was somewhat unexpected. In cementitious systems, the negatively charged sulfate is known to be in a competitive adsorption with SPs, which reduces the SP adsorption (Yamada et al., 2001). Such behavior was observed in a similar setup with pure cement. Both setups are prone to  $\text{CaSO}_4$  precipitation, which reduces the available sulfate in the solution. As cement has a much lower specific surface area than the used illitic clays, precipitation of  $\text{CaSO}_4$  in a CC system might prevent full surface coverage with sulfate. Additionally, the used SP 52HPEG6 has a high anionic charged density  $2146 \mu\text{eq/g}$  (Table 4) (Plank and Sachsenhauser, 2009), which may have negated the competitive adsorption with sulfate ions. In any case, competitive adsorption of SP and sulfate could not be confirmed for all CCs in the present study.

Spósito et al. (2020) indicated the specific surface area as a solid indicator for determining general flowability. The linear regression of SP adsorption of the CCs after calcium addition and specific surface area in Figure 9-a proved this true once more. It provided a high correlation  $r^2 = 0.88$  for all CCs (Kundt et al., 2011). But taking into account only illite containing CCs the correlation is reduced to a  $r^2 = 0.69$ , which can be

considered really low since it included only three data points. This was not surprising since cIIIE and cIIIA had very similar specific surface areas, but quite different behaviour in regard to SP adsorption and their rheological behavior. So, it can be concluded, that specific surface area cannot be a sole parameter to differentiate SP adsorption or rheological parameters in general within illitic CCs.

Correlating SP adsorption of the CCs after calcium addition with the difference in zeta potential (before and after calcium addition in Figure 6-b) led to a low correlation (Figure 9-b). Obviously, this is not a good indicator for CCs in general. Isolating the correlation to only illitic CCs, a very high correlation of 0.95 occurred, with the aforementioned limitation of only three data points being available. So, specific surface area is a solid indicator for CCs in general, but has its limits when it comes to comparison within a clay mineral type. For a differentiation within a clay mineral, zeta potential may be a good indicator. For a correlation of SP adsorbed on CC surfaces between smectitic and illitic CCs, zeta potential is not sufficient.

As shown earlier, SP adsorption is highly depended on calcium-saturated surfaces. Specific surface area and difference in zeta potential are both parameters that are indicators for calcium uptake. The more surface area is available, the more calcium ions can adsorb. The higher difference in zeta potential is, the denser the surfaces can be populated. The mineralogy and especially, the type and quantity of clay minerals are the most relevant factors for different characteristics such as zeta potential and specific surface area. Therefore, mineralogy seems to play a key role in SP adsorption.

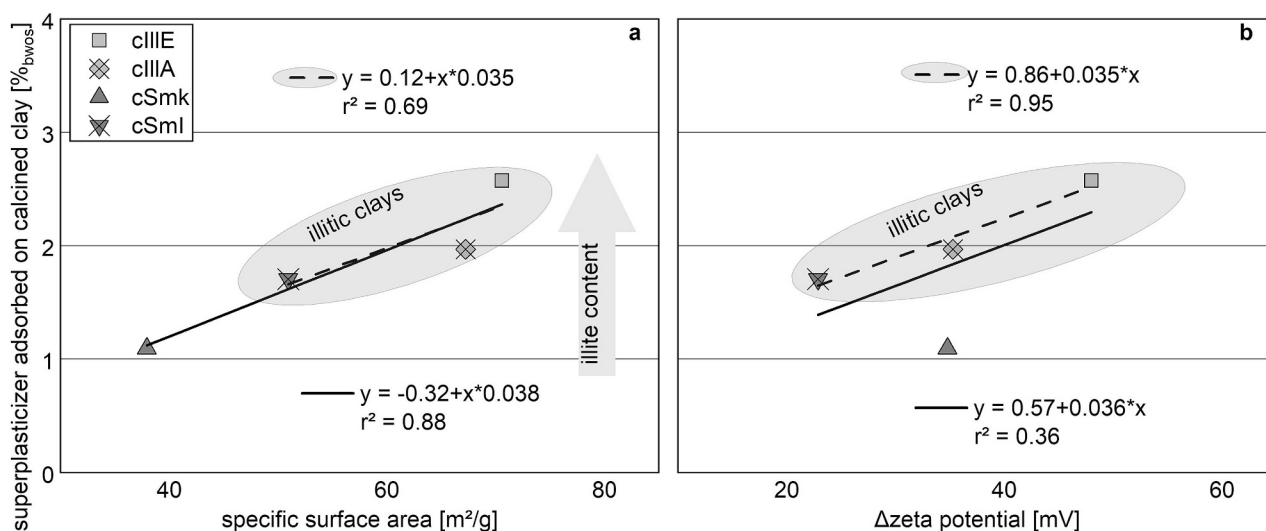


**Fig. 9.** Superplasticizer (SP) adsorption on calcined clay (CCs) after calcium addition correlated with BET specific surface area (a) and correlation with the difference (Δ) in zeta potential before and after calcium addition in potassium hydroxide solution (KOHs) (b). Dashed lines are correlations using illitic calcined clays (CCs) only.

#### 4. Conclusion

This research investigated four calcined clays with main constituents illite and smectite in cement-free aqueous solutions to gain a deeper understanding of their influence on superplasticizer interaction and rheology in general in cementitious systems. The following conclusions can be drawn:

- An increase in calcined clays' yield stress when switching from deionized water suspension to synthetic cement pore solution was likely caused by a reduction in osmotic repulsion force due to lower absolute values of the zeta potential and higher ion concentration. Ettringite formation was not detected and therefore, its influence on the yield stress can be ruled out.
- Calcined clays adsorb calcium ions onto their negatively charged surface, leading to a change to positive polarity. Sulfate adsorption on calcium-saturated surfaces seemed less significant.
- Anionic superplasticizer can adsorb on negatively charged calcined clay surfaces. Calcium saturation of calcined clay surfaces increased superplasticizer adsorption drastically. Unlike in cement systems, competitive superplasticizer – sulfate adsorption seemed to play a subordinate role.
- Calcined smectite is not an issue for cement concerning rheology in clay suspensions. Its water absorption capacity was halved due to calcination. Swelling and superplasticizer side chain intercalation were not possible after calcination. Superplasticizer adsorption on the calcined smectite was considered low in comparison to calcined illitic clays.
- BET specific surface area can be a good first indicator for superplasticizer demand. Within one mineralogy, zeta potential might be a more reliable indicator. Both parameters are related to the amount of calcium that can be adsorbed onto calcined clay surfaces, which likely is key factor governing superplasticizer adsorption.

In future, interaction of superplasticizers and pore solution needs to be tested in cementitious systems, especially with a focus on slump retention to achieve sustainable, but also workable concrete using calcined clays.

#### CRedit authorship contribution statement

**Axel Neißer-Deiters:** Writing – original draft, Methodology, Investigation. **Sebastian Scherb:** Writing – review & editing, Methodology, Investigation. **Nancy Beuntner:** Writing – review & editing. **Karl-Christian Thienel:** Writing – review & editing, Supervision.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.clay.2025.108101>.

#### Data availability

Data will be made available on request.

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