INTRODUCTION

Calcium sulfates take an important role in the reaction of pozzolanic materials by forming ettringite with aluminum ions from the pozzolan. Sulfate carriers like gypsum, bassanite, or anhydrite are used to retard the tricalcium aluminate (C₃A) reaction in ordinary portland cement (OPC). The latter mechanism is used to avoid a superposition of the silicate and aluminate clinker reaction. As calcined clay blended cements or limestone calcined clay cements (LC₃) are currently among the most promising solutions to address CO₂ emissions in cement industry, their influence on cement hydration in general and on the aluminate reaction in particular is gaining attention. In calcined clay blended cements, where additional aluminum sources are present, awareness has been raised for extra sulfate demand, as the

Hydration of cubic tricalcium aluminate in the presence of calcined clays

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Abstract
Calcined clay blended cements play a major role in cement industry’s strategy to reduce CO₂ emissions. During their hydration, an accelerated aluminate reaction is often observed to affect the sulfate balance. The objective of this study was to provide insights into the influence of different calcined clays on the hydration of cubic tricalcium aluminate (C₃A). A cementitious model system consisting of cubic C₃A, quartz powder, calcium sulfate and a model pore solution was investigated. The influence of three different calcined clays and one nanolimestone was examined by a successive replacement of the quartz powder and variation of the calcium sulfate. Heat flow and hydrate phase development were followed by isothermal calorimetry and quantitative in-situ X-ray diffraction. Accelerated ettringite formation and sulfate depletion were observed for all calcined clays, while the nanolimestone exhibited the opposite effect.

It was found that adsorption of SO₄ ions and/or Ca-SO₄-complexes at the surface of calcined clay particles is the main factor inhibiting retardation of the C₃A hydration in absence of a silicate reaction. In the Al-rich systems a retardation through sulfate adjustment seems to be impeded by additional Al ions, which react with Ca adsorbed onto and leached from the C₃A surface.

KEYWORDS
calcined clay, metakaolin, sulfate, supplementary cementitious material, tricalcium aluminate, X-ray diffraction
C₃A and alumina-rich calcined clay minerals might compete for the sulfate at the solid-liquid interface. Several studies have proven that alumina from metakaolin can contribute to ettringite formation. Hence, in blends of cement and calcined clay there is a risk of undersulfation. An enhanced ettringite formation during the dormant period as well as an acceleration of the sulfate depletion is often observed. While some studies refer to the additional aluminum ions to explain aforementioned effects, a recent work suggests the high specific surface area (SSA) of calcined clays as the driving force. The faster aluminate reaction was correlated to the acceleration of the silicate reaction, which is driven by the filler effect. As SO₄²⁻ ions adsorb on the newly formed calcium silicate hydrate phase (C-S-H), an accelerated C-S-H formation speeds up the adsorption of sulfate and thus the sulfate depletion peak. The role of ion adsorption during early cement hydration has gained increasing significance in recent research, especially regarding the aluminate reaction. While the retardation of the C₃A reaction has been traditionally attributed to a diffusion barrier formed by ettringite on the C₃A surface, more recent studies suggest adsorption of calcium and sulfate ions on C₃A, where they hinder dissolution. The fact that the C₃A reaction rate increases before the ettringite consumption by AFm phases begins, as well as the morphology of ettringite, which seems to be unsuitable as a diffusion barrier, support this theory. Geng et al. proved the high porosity of the ettringite needle network at the C₃A reaction front using X-ray ptychography and transmission X-ray microscopy, which rules out any effect as a physical barrier. Myers et al. identified adsorbed Ca-sulfur ion pair complexes onto an “Al-rich leached layer,” formed at the C₃A surface, as the key inhibitors of its dissolution. Liu et al. demonstrated that it requires a coexistence of calcium as well as sulfate ions to retard the aluminate reaction. Joseph et al. combined both theories by suggesting that not only calcium and sulfate ions block the active surface but also ettringite—explicitly not as a diffusion barrier. Even though the described theories are still under debate and the mechanisms not fully understood, there is a consensus regarding adsorbed ions as the key inhibitor of the C₃A reaction.

Raw clays and soils are well known for their adsorption capacity of organic and inorganic solutes. The sulfate adsorption capacity of soils is depending, inter alia, on clay content, nature of clay minerals, and pH. Lei & Plant could prove the adsorption of large amounts of Ca⁴⁺ onto the surface of clay particles by measuring a strong increase of the initially negative Zeta-potential of muscovite, kaolinite and montmorillonite in Ca⁴⁺ titrated suspensions. Similar observations were made with a calcined kaolinitic clay. There is however lack of data, which could prove adsorption of SO₄²⁻ or Ca-SO₄ ion pair complexes onto the surface of (calcined) clay particles.

The objective of this study on reduced cementitious model systems was to investigate the influence of calcined clays on the early hydration of C₃A in the presence of calcium sulfate. The effects of sulfate content as well as type and amount of calcined clay, which affects SSA and amount of dissolved aluminum, are studied. A quantitative inspection of phase development in combination with isothermal calorimetry should point out if supplementary cementitious materials (SCM) with high SSA and additional aluminum ions have the potential to accelerate the aluminate reaction independent of C-S-H formation. The work intends to discuss the role of ion release and ion adsorption of calcined clay minerals and their influence on the hydration of C₃A.

## 2 | EXPERIMENTAL PROCEDURE

### 2.1 | Cementitious model System

A reduced cementitious model system based on synthetic C₃A was developed. Therefore, cubic C₃A was synthesized by sintering of CaCO₃ (Sigma Aldrich, 99.95%) and Al₂O₃ (Acros, 99.99%) in stoichiometric balanced ratio. The homogenized educts were calcined for 16 h at 1000°C and sintered twice for 6 h at 1400°C in a laboratory muffle furnace with intermediate grinding and homogenization. The final product was ground two times for 5 min in a rotary disc mill (Retsch RS200) using a tungsten carbide grinding tool and sieved through a 63 µm sieve. The purity of the C₃A was verified by XRD (Figure 1) and found a quantity of 98.5 wt% C₃A together with 1.5 wt% mayenite.

Three calcined clays were chosen for investigation: A fine kaolinitic clay (70.6 wt% kaolinite, high disorder) calcined at 650°C, referred to as CKf, a coarse kaolinitic clay (78.2 wt% kaolinite, low disorder) calcined at 700°C, referred to as CKc and an illitic clay calcined at 770°C, referred to as CI. Calcination was performed in a preheated laboratory muffle furnace for 30 min. The calcination temperatures were chosen following previous studies on pozzolanic reactivity. The calcined clays were ground for 10 min in a rotary disc mill using an agate grinding tool. Additionally, a nanolimestone (Skyspring Nanomaterials, Inc.), referred to as nLS, which provides high SSA but neither reactive silicon nor aluminum ions, was investigated solely by isothermal calorimetry to examine the pure effect of surface area. The mineralogical composition of the calcined clays and the nLS was determined by Rietveld refinement and is given in Table 1. Amorphous content was calculated following the external standard method. Gypsum from Merck with a purity of >99% was used as provided by the producer. A verification of the phase composition by XRD gave a mass proportion
of 25.0 wt% bassanite. Since this amount is considered sufficient as early available sulfate source, no further bassanite was added. Hereafter, the sulfate carrier in the given ratio will be referred to as CS̅. Table 2 provides the chemical composition, loss on ignition (LOI), mass attenuation coefficient (MAC), SSA and median particle diameter (d50) of all used materials. The MACs were calculated from the chemical composition using the MACs of the single elements provided in International Tables for Crystallography for Cu Kα radiation.35 Furthermore, zeta potential is given determined by electroacoustic measurement in a mixed hydroxide solution (MOH)36 at a solid content of 25 wt%. MOH solution was used during all experiments in order to imitate a cementitious pore solution on one hand and to generate a reactive environment for the calcined clays by providing a sufficiently high pH on the other. The solution is composed of 50 mmol/l NaOH and 300 mmol/l KOH and possesses a pH of 13.57. A lime solution was intentionally not used, in order to impede C-S-H formation, which might affect the results. With the aims of reducing heat release and simulating the surface of OPC, the C3A content was kept constant at 10 wt% in all mixtures by filling it up with quartz powder, which provides a surface area and particle size distribution comparable to OPC. A basic test series with varying CS content was examined in order to establish a reference system (C3A_xCS̅; x = 2, 3, 4, 5, 6). Two test series were examined successively for each calcined clay. The first one investigates the influence of the replacement level of the calcined clays and the nanolimestone. The second one considers the variation of the sulfate carrier at a constant calcined clay content. The notation C3A_5CS̅_20CKc e.g. refers to a sample consisting of 10 wt% C3A, 5 wt% sulfate carrier, 20 wt% CKc and 65 wt% quartz powder. All experiments were conducted at a liquid to solid ratio of 0.6. A summary of all investigated systems is provided in Table S1.

### 2.2 Evaluation of chemical reactivity

To evaluate the chemical reactivity of the single calcined clays, the soluble silicon and aluminum ions in MOH were determined after 6 and 24 h according to Beutnner and Thienel.36 1 g of the sample was eluted in 400 ml MOH on an interval agitator. The eluate was filtered and acidified to a pH of 1.0 after the corresponding time. The concentration of silicon and aluminum ions was measured using ICP-OES (Varian ICP-OES 720 ES) as described by Scherb et al.37 A multi-point calibration with an external standard was carried out beforehand. Assessment of chemical reactivity according to current state of the art was performed by determining the evolved heat during the first 72 h using the R3 calorimetry test.38,39

### 2.3 Heat flow calorimetry

Heat flow measurements were conducted in the model system (see Section 2.1) at 25°C in a TAM Air isothermal
calorimeter from TA instruments. Pastes were prepared manually by external stirring for 60 s and approx. Two gram of homogenized paste was transferred into a flask. The flasks were inserted into the calorimeter within 2 min after water addition. Quartz powder and deionized water were used in a ratio of 2:1 as reference substance.

### 2.4 | X-ray diffraction

In situ XRD experiments of selected systems were performed with a PANalytical Empyrean diffractometer (CuKα, Bragg–BrentanoHD monochromator, PIXcel1D linear detector) in order to quantify the phase development during hydration. For this purpose, the samples were mixed manually and transferred into a sample holder, which was placed onto a temperature controlled sample stage at 25°C and covered with a 7.5 µm Kapton film. Measurements were carried out at 40 kV and 40 mA for 24 h with a time resolution of 15 min per scan. Rietveld refinement was employed for each scan using Profex-BGMN. The scattering contribution of the Kapton film was modeled using the measurement of a silicon single-crystal sample carrier covered with a Kapton film. The scale factors of the single phases were extracted to calculate the absolute amounts of the crystalline phases by applying the external standard approach. Recrystallized zircon was used as external standard. The crystal structures, which were applied for Rietveld refinement are given in Table 3. Monosulfate (C₄AS₉ x H₁₄₄) was refined using the crystal structure of kuzelite, modified with lattice parameters for C₄AS₉ x H₁₄₄. The problems regarding quantification of AFm phases are reported elsewhere. The gypsum used in the experiments showed strong preferred orientation during the in-situ measurements, which led to a slight overestimation in Rietveld refinement. This was taken into account by normalizing the retrieved quantities to the maximum theoretical gypsum content. Samples for XRD measurements after 7 days of hydration were prepared analogously to in-situ measurements. The samples were covered and sealed with a Mylar film, placed in a drying cabinet at 25°C for exactly 168 h and measured under the same conditions as the in situ measurements.

### 2.5 | Scanning electron microscopy

Samples for scanning electron microscopy (SEM) were prepared analogously to Section 2.3 and stored in a sealed plastic container in a drying chamber at 25°C. After 24 h, a fraction of the sample was glued on a sample holder and coated with gold. Secondary electron images were taken in a Zeiss Evo LS 15 at 20 kV and a working distance of 8.5 mm.
2.6 | Thermodynamic modelling

Phase assemblage at thermodynamic equilibrium was calculated using the Gibbs free energy minimization software GEMS\(^{51}\) in combination with the databases PSI-GEMS\(^{52}\) and Cemdata18\(^{53}\). Input recipes were created using the mass proportions of the respective XRD and calorimetry experiments. The conditions for the simulations where set analogous to the experiments at ambient pressure and 25°C. Phase assemblage of the reference system was calculated depending on CS\(^{-}\) content. For the system substituted with 20 wt% calcined kaolinitic clay, the reaction degree of metakaolin was varied in a range which is consistent with data from literature.\(^{37,54}\)

3 | RESULTS AND DISCUSSION

3.1 | Chemical reactivity of the calcined clays

The investigated calcined clays exhibit different chemical reactivity during the first 24 h (Figure 2). CKf reveals the fastest release of Si and Al ions in MOH as well as the fastest heat release in the R\(^3\)-test during the first 22 h. CI exhibits the overall lowest chemical reactivity, even though the amount of released Si ions after 6 h is slightly higher as for CKc. CKc shows a slow reactivity in the R\(^3\)-test during the first 6 h, which then accelerates and exceeds the evolved heat of CKf after approximately 22 h. However, after 24 h only half the amount of Al and Si ions are released as compared to CKf. The lower chemical reactivity of calcined illite as well as the higher ratio of Si to Al ions in comparison to calcined kaolinitic clay is in line with previous publications.\(^{32,55,56}\) The slower reaction rate of CKc compared to CKf can be explained by lower specific surface area and degree of disorder in the kaolinite structure.\(^{31,55,57}\) The fact that the evolved heat of CKc exceeds CKf after 22 h results from the higher calcined kaolinite content of CKc. The still lower solubility of CKc compared to CKf after 24 h can be attributed to the lower pH of the MOH solution compared to the R\(^3\) system and to the fact, that the one represents a reacting system and the other a straight dissolution process.

3.2 | C\(_3\)A-systems without calcined clays

The reference system was chosen considering the following conditions: The amount of sulfate should be sufficient for a complete transformation of C\(_3\)A into monosulfate without significant formation of CAH phases at thermodynamic equilibrium. This holds for a minimum CS\(^{-}\) content of 5 wt% (Figure 3). Beyond that, a distinct and reproducible heat flow maximum should be present. Figure 4 exhibits the course of the heat flow of the C\(_3\)A hydration reaction in absence of calcined clays depending on the CS\(^{-}\) content. The first exothermic peak is not completely recorded due to the external sample preparation. The smaller initial maximum of the systems with lower sulfate content can therefore be explained by an already higher heat release during sample preparation. Pourchet et al.\(^{58}\) have shown, that the intensity of this peak is independent of the amount of sulfate added but certainly depends on the type of sulfate carrier. The second heat flow maximum, which can be attributed to the sulfate depletion, shifts to later times with increasing sulfate content together with a significant decrease in peak height and increase in peak width. This effect was observed already by other authors\(^{25,59,60}\) and

![Figure 2](image-url) | Figure 2: Evolved heat during R\(^3\) calorimetry test and solubility of Al (relative standard deviation (RSD) = 11%) and Si (RSD = 10%) ions in alkaline solution during the first 24 h

![Figure 3](image-url) | Figure 3: Thermodynamic stability in the reference system depending on the CS\(^{-}\) content calculated in GEMS [Color figure can be viewed at wileyonlinelibrary.com]
can be explained by an extended time for the removal of calcium, sulfate and possibly ettringite from the C₃A surface. The system C₃A₅CS was chosen for the further investigations. The phase development and the heat flow during the first 24 h of hydration are presented in Figure 5A. The in-situ XRD measurements (Figure S1) reveal that bassanite is not detectable anymore during the first scan of the measurement, as it immediately dissolves. Taking into account, that the theoretical C₃A content before the start of the reaction is 6.25 wt%, a significant initial dissolution of about 2.5 wt% takes place, which is not surprising, regarding the high liquid-to-C₃A ratio. In comparison, an immediate dissolution of 1.8 wt% of initially 6.9 wt% was observed. The amount of dissolved C₃A is higher at every point of time than the amount that is needed for the precipitation of the corresponding hydrate phases. The difference could partly be dissolved in the pore solution or bound in AFm gel as described by Geng et al. They observed ‘gel-like’ areas intermixed with ettringite needles at an early age of hydration. Jansen et al. could not detect significant amounts of amorphous phase and therefore attributed the difference to Al adsorbed on the surface. After the initial dissolution, the C₃A content stays almost constant until the depletion of the gypsum. At this point of time, the maximum ettringite content (6 wt%) is reached, which is significantly lower than the theoretical value (8 wt%) based on the CaSO₄ content. As the gypsum depletes, ettringite is consumed and monosulfate (C₄AS₅ x H₁₄) forms. The major part of the monosulfate formation still falls into the stadium, where the reaction kinetic is defined by the C₃A dissolution. The heat flow maximum correlates with the maximum C₃A dissolution rate, which is in line with the well-known fact that the accelerated C₃A dissolution after sulfate depletion is the primary reason for the enhanced heat development. After 24 h, approximately 0.8 wt% C₃A are left while 2.8 wt% ettringite and 3.3 wt% monosulfate have formed. For these reactions 2.0 wt% C₃A are needed, which are already provided by the initial dissolution. The dissolution of almost 3.5 wt% of C₃A cannot be explained at this stage, even though if part of it could be caused by an underestimation of AFm phases in Rietveld analysis, due to their low crystallinity, which has already been reported elsewhere. 

**FIGURE 4** Course of heat flow for different sulfate contents in the C₃AₓCS₅-system [Color figure can be viewed at wileyonlinelibrary.com]

**FIGURE 5** Heat flow curves and phase development for the systems with 5 wt% CS₅; A) without and B-D) with 20 wt% calcined clay (initial C₃A contents are marked by the green crosses; the symbols correspond to results of two individual measurements, the lines represent the average) [Color figure can be viewed at wileyonlinelibrary.com]
3.3 | C\textsubscript{3}A-systems in presence of calcined clays

3.3.1 | Acceleration of the hydration

The addition of 20 wt% calcined clay (CI, CKf, CKc) has a massive impact on the reaction kinetics as sulfate depletion and ettringite formation are accelerated significantly (Figure 5, Figure S2). While the formation of ettringite until its maximum content evolves in two steps in the system C\textsubscript{3}A\_5C\textsubscript{S}, it forms continuously in the systems with calcined clay. C\textsubscript{3}A\_5C\textsubscript{S}\_20CKf and C\textsubscript{3}A\_5C\textsubscript{S}\_20CI exhibit an acceleration of the sulfate depletion from 6 h down to approximately 2 h. In the course of the heat flow, the first and the second maximum coincide, leaving only a small second heat maximum, which appears after 4 h for CI and after 6 h for CKf. CKc causes a less pronounced acceleration, leaving the two reaction maxima still visible. The systems with calcined clay reach—or in the case of CKc almost reach—the theoretical maximum ettringite content of about 8 wt\% (based on the CaSO\textsubscript{4} content). However, there is a significant difference in the consumed C\textsubscript{3}A between the different systems. After sulfate depletion, no further decline in C\textsubscript{3}A content takes place in the systems C\textsubscript{3}A\_5C\textsubscript{S}\_20CKc and C\textsubscript{3}A\_5C\textsubscript{S}\_20CI. In the system with CKf the C\textsubscript{3}A dissolves continuously and strätlingite (C\textsubscript{2}ASH\textsubscript{8}) begins to form after 6 h. This correlates well with the solubility (Figure 2), which is still lower for CI and CKc after 24 h as for CKF after 6 h.

The acceleration phenomenon could be explained in the first instance by three arguments:

1. The calcined clays provide extra aluminum ions. Therefore, the tricalcium aluminate and the calcined clay minerals compete for the sulfate, which leads to an undersulfation of the system and accelerated ettringite formation.\textsuperscript{7} If this was the case, CI would show the lowest acceleration, since it provides the lowest amount of soluble aluminum ions.

2. The acceleration is mainly driven by the filler effect.\textsuperscript{63} The high specific surface area of the dehydroxylated clay minerals provides additional nucleation sites for ettringite and/or monosulfate formation. Figure 6 shows an exponential correlation between specific surface area of the systems containing calcined clays, which was varied by using different replacement levels, and the heat flow maximum during isothermal calorimetry (sulfate depletion peak (SDP)). The higher the SSA the smaller the reaction time. The curves for the systems with different calcined clays however differ clearly between each other. This fact could be interpreted as a coupled influence of SSA and aluminum solubility. In order to verify this theory, the effect of a simple increase of surface area was investigated by substituting the calcined clays by nLS. Surprisingly on a first glimpse, the addition of nLS leads to a retardation of the reaction (Figure 6). The SSA of nLS is comparable to that of CKc. If physical effects were dominant, nLS and CKc would show a similar acceleration.

3. The Ca\textsuperscript{2+} and SO\textsubscript{4}\textsuperscript{2−} ions adsorb on the surface of the clay minerals. The decisive factor therefore, besides the specific surface area, is the surface charge. In the case of C\textsubscript{3}A, ion pair complexes adsorb on a negatively charged aluminum-rich leached layer and inhibit the hydration.\textsuperscript{22} Clay minerals could fulfill these conditions as well. Regarding 2:1 clay minerals, oxygen atoms of the tetrahedral sheet build up the basal surface. Isomorphous substitutions of Al for Si create a negative surface charge,\textsuperscript{64} which also applies for the tetrahedral sheet in kaolinite.\textsuperscript{65} Based on the average structural formula for illite, Al substitutes 20% of tetrahedral Si.\textsuperscript{66} This means, that the basal surface of 2:1 clay minerals provides Al-rich sites with negative charge, where complexes of Ca and SO\textsubscript{4} might adsorb comparable to C\textsubscript{3}A. This accounts as well for kaolinite, where the silica facet is charged negatively at pH ≥4 and the gibbsite facet at pH >7.\textsuperscript{67} Even though, the gibbsite layer gets distorted during dehydroxylation together with a change of Al-coordination from 6-fold to 5- and 4-fold, we still assume a negative charge of this sheet.

These hypotheses are supported by the zeta potentials provided in Table 2. CKf shows the highest negative value, followed by CI and CKc. Regarding the high SSA of the calcined clays in comparison to C\textsubscript{3}A, the assumption of a much higher adsorption capacity of the former compared...
to the latter seems reasonable which would explain the massive acceleration of the C₃A hydration. Consequently, no, or at least significantly lower adsorption occurs on the surface of calcite particles. The Zeta potential of limestone in the presence of CaSO₄ and different alkali-sulfates and -hydroxides was found to be notably higher in comparison to ground quartz, which could explain the retarding effect observed when substituting quartz with nLS. However, the measured value in MOH (in absence of CaSO₄) is comparable to that of quartz, so there might be further effects that lead to the retardation, for example, change of thermodynamics due to partial calcite dissolution or adsorption of nanoparticles on the C₃A as already observed for nanosilica.

The authors promote the third option. As Figure 6 demonstrates, the influence of SSA is clearly present. However, there are strong differences between the single calcined clays and the nLS. The systems with CKc and CKf exhibit a significantly faster sulfate depletion compared to CI at identical SSA (Figure 6). This cannot be drawn back to additional supply of Al ions, as CKc only provides slightly more Al ions than CI after 6 h (Figure 2).

We therefore assume that the used calcined kaolinite provides a higher negative surface charge than the calcined illite and thus a higher adsorption capacity for Ca²⁺ and SO₄²⁻. This is however just partly reflected in the zeta potentials as only CKf exhibits a stronger negative value than CI. Lei & Plank proved the adsorption of a large amount of Ca²⁺ onto initially negative charged surfaces of muscovite, kaolinite and montmorillonite. They could further point up, that this charge reversal of clay particles also appears in synthetic cement pore solution. In cementitious systems, the zeta potential increases with the Ca/SO₄ ratio. Liu et al. emphasize the availability of both Ca and SO₄ for inhibiting the C₃A dissolution. In the present work, C₃A and CaSO₄ are the only soluble Ca-sources, resulting in a lack of Ca ions in the pore solution compared to true cementitious pore solutions. Consequently, no conclusion can be made whether it is the lack of Ca²⁺, SO₄²⁻ or both, which impedes an inhibition of C₃A dissolution during the first hours in the calcined clay substituted systems. Nevertheless, it can be concluded that adsorption mechanisms on the surface of the calcined clay particles are the driving force for the accelerated C₃A hydration. The described mechanism is in line with the theory, that adsorption mechanisms play the essential role in the retardation of C₃A hydration.

### 3.3.2 | Phase assemblage

Both SEM images in Figure 7 show intergrown prismatic ettringite crystals. In the left area of Figure 7A, the quartz surface is visible, indicating it does not serve as nucleation area for ettringite. In the depicted area of sample C₃A_5CS₂₀CKf (B) a denser structure with prismatic and platy crystals is shown of which the latter crystals might represent strätlingite. These crystals seem to nucleate and grow on the surface of the calcined clays. If Al and Si ions are added with calcined clay, the thermodynamic stability shifts from monosulfate to ettringite and strätlingite (Figure 8). Formation of strätlingite is known from metakaolin blended systems, when the metakaolin/portlandite ratio is above 1 and the C-S-H can no longer incorporate aluminum. Figure 8 shows the thermodynamic stable phase assemblage for a system with 5 wt% CS and 20 wt% calcined clay depending on the degree of metakaolin reaction. At a reaction degree of 22 g reacted metakaolin per 100 g calcined clay, monosulfate is not stable anymore. Based on the solubility experiments in the MOH solution, the reaction rate after 24 h is 16.0 g reacted metakaolin per 100 g of calcined clay, monosulfate is not stable anymore. The strätlingite precipitation is often kinetically delayed in cementitious systems, which
explains the retarded formation in the systems examined here. In the systems C₃A₅CS̅₂₀CKc and 20CI, the hydration of C₃A seems to break down once the maximum ettringite content is reached and no formation of strätlingite is visible. To verify this, the samples were investigated by XRD after 7 days of hydration (Figure 9). While in the Ref 5% system ettringite and C₄AS̅xH₁₄ have further reacted to C₄AS̅xH₁₂, ettringite stays stable in all substituted systems and strätlingite has formed. The calcite content in CI leads to the formation of hemicarboaluminate. As CKf provides the fastest release of silicon ions (Figure 2), the strätlingite formation takes place earlier and more rapidly than in the other systems.

### 3.4 Sulfate adjustment

CS̅ content was increased stepwise, in order to retard the C₃A hydration (Figure 10). In the systems with CKc this results in a split-up of the heat flow into three maxima. In the Cl-systems, the increase in CS̅ leads to a broadening and reduction of intensity of the heat flow maximum. With an addition of 20 wt% CS̅, the initially sharp heat flow peak begins to form a shoulder. The CKf system allows no retardation at all. The only effect is an increase of intensity and a small

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**FIGURE 8** Computed phase assemblage in the investigated model system with 5 wt% CS̅ and 20 wt% calcined kaolinitic clay depending on the amount of reacted metakaolin [Color figure can be viewed at wileyonlinelibrary.com]

**FIGURE 9** XRD patterns of C₃A₅CS̅ and the systems with 20 wt% calcined clay after 7 days of hydration (Str = strätlingite, Ett = ettringite, MS = monosulfate, Hc = hemicarboaluminate)

**FIGURE 10** Heat flow depending on CS̅ content in the systems (A) with CKc, (B) with Cl and (C) with CKf (note the different scale of the ordinates) [Color figure can be viewed at wileyonlinelibrary.com]
broadening due to the higher amount of ettringite formation. At an addition of 20 wt% C₅S, a small shoulder begins to appear.

In the systems with the maximum C₅S content (C₃A_20C₅S_20CI, C₃A_20C₅S_20CKf and C₃A_10C₅S_20CKc), in situ XRD measurement were carried out (Figure 11). In the system C₃A_20C₅S_20CI, the reaction of C₃A is inhibited after 2.8 h. The formation of ettringite proceeds at two different rates. A rapid ettringite formation appears parallel to a fast gypsum and C₃A dissolution until 2.8 h. Subsequently, gypsum dissolution and ettringite formation slow down, while C₃A dissolution stops. It can be deduced, that the inhibition of C₃A dissolution slows down the ettringite formation, which however continues at low level during the remaining measuring time. Since a further dissolution of C₃A during this time is not detectable, the required aluminum might origin from the calcined illite or from amorphous AFm gel as described in Section 3.2. Geng et al. described the AFm gel to be unstable and “feed the precipitation of ettringite during the low-reactivity period”. This corresponds with the described observations. In the system C₃A_20C₅S_20CKf, C₃A and gypsum dissolution as well as ettringite formation proceed significantly more rapidly. The C₃A consumption breaks down at the same time as in the CI system, even though nearly three times the amount of ettringite has precipitated in comparison at this point of time. This proves once more, that the amount of precipitated ettringite does not influence the inhibition of the C₃A hydration, which corresponds to the theory of adsorbed ion pair complexes as key inhibitor.²² Regarding the time between 4 and 12 h, 0.4 wt% of C₃A and 3.0 wt% of gypsum are consumed, while 4.2 wt% of ettringite are precipitated. Only 1.7 wt% of gypsum but 0.9 wt% of C₃A would have to be consumed for the formation of this amount of ettringite. This indicates again that another aluminum source has to be present at this point of time. The fact that during this time range more calcium sulfate is consumed than precipitated suggests that the adsorption of calcium and sulfate continues. Moreover the Ca²⁺ ions from the additionally dissolved gypsum could serve as a reaction partner for a calcium-free aluminum source such as calcined kaolinite. After 24 h, 28.1 wt% of ettringite are formed. The theoretical ettringite maximum is 28.5 wt% based on C₃A as well as gypsum consumption. This suggests in the first instance, that the aluminum ions of the calcined kaolinite are not involved at this point of time, which supports the theory of an intermediate AFm formation. Regarding the system C₃A_20C₅S_20CKc, three different phases of ettringite precipitation can be identified. The first one is fed by initially dissolved C₃A, as no more C₃A is dissolved in parallel. After 2.0 h, ettringite formation slows down, while gypsum is consumed at a low rate and C₃A stays constant. Between 5 and 8 h, a second reaction maximum appears, which goes along with accelerated sulfate consumption and ettringite precipitation. In this time range further 0.4 wt% of C₃A are dissolved. Between 8 and 20 h the reaction continues on a low level with slowed down sulfate consumption and ettringite formation. A third maximum with another accelerated ettringite precipitation rate is indicated after 20 h. Even though CI and CKf exposed a quite similar reaction behavior in the presence of 5 wt% C₅S, they behave remarkably different when the sulfate content is increased stepwise (Table 4). This could be drawn back to the difference in chemical reactivity of the calcined clays and the Al-rich leached layer of the C₃A. In

**FIGURE 11** Heat flow curves and phase development for the systems with 20 wt% calcined clay and maximum sulfate dosage; the symbols correspond to results of two individual measurements, the lines represent the average (note the different scale of the ordinates) [Color figure can be viewed at wileyonlinelibrary.com]
consistency with the Al-rich leached layer theory, there is lack of Al at the C₃A/solution interface as compared to Ca with respect to ettringite formation. Consequently, precipitation of ettringite is slowed down. The Al ions released by the calcined clay at this point of time—which are about three times more for CKf as compared to CI—could then serve as reaction partner for the Ca, leached from the surface of the C₃A or adsorbed on the Al-rich leached layer, with the result of a restarting C₃A-dissolution.

4 | CONCLUSION

The results at hand are in the first view in line with previous publications regarding the dominating effect of surface area on the accelerated sulfate consumption in blended cementitious systems. However, they strongly indicate that SO₄ ions and/or Ca-SO₄-complexes can adsorb immediately on the surface of negatively charged calcined clays, depending on surface charge and area. This leads to an acceleration of the sulfate depletion, as the Ca and SO₄ ions are not available to retard the C₃A dissolution. This process, which has previously been exclusively attributed to C-S-H, can thus also take place in absence of C₃S hydration. The authors are aware, that the results obtained here cannot be simply transferred to real cementitious systems, as the presence of C₃S influences the C₃A hydration and vice versa. However, they indicate that the accelerated aluninate reaction in calcined clay blended cementitious systems, can neither be traced back exclusively to the accelerated silicate reaction nor to the additional aluminum ions. A nanolimestone showed the opposite effect as compared to the calcined clays. Obviously, calcined clay minerals play an active role in adsorbing ions from the pore solution and can thereby affect hydration beyond the previously known chemical and physical effects. A secondary source of early available Al seems to inhibit the retardation of the C₃A reaction by further addition of sulfate carriers. This was drawn back to a reaction of the Al provided by the calcined kaolinite with the Ca leached from or adsorbed on the Al-rich leached layer of the C₃A, disabling the mechanisms which inhibit C₃A dissolution. The observations support the theory of adsorbed ion pair complexes as key inhibitor of the aluninate reaction, as enhanced early ettringite formation was not observed to slow down C₃A dissolution. While the thermodynamic calculations revealed valuable information about phase assemblage of the investigated systems at equilibrium, following studies might also use numerical models to simulate reaction kinetics. As the hydration studies were performed in absence of Ca(OH)₂ and silicate clinker phases, their influence needs to be addressed in future experiments.

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TABLE 4 Evolved heat of the systems with 20 wt% CKf and CI and different amounts of C₃S

|               | Evolved heat (J/g) |
|---------------|--------------------|
| Time [h]      |                    |
| C₃A_5CS      | 16.0 59.4 69.3     |
| C₃A_5CS₂₀CKf | 44.0 60.0 68.6     |
| C₃A_10CS₂₀CKf| 76.7 82.2 85.0     |
| C₃A_2₀CS₂₀CKf| 122.0 132.7 133.2  |
| C₃A_5CS₂₀CI  | 48.3 64.0 76.6     |
| C₃A_10CS₂₀CI | 64.7 75.2 78.8     |
| C₃A_2₀CS₂₀CI | 74.2 83.2 85.9     |
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