

# PARAMETERS INFLUENCING THE ALUMINATE CLINKER REACTION IN PRESENCE OF CALCINED CLAY: IMPLICATIONS FROM MODEL SYSTEMS AND BLENDED CEMENTS

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## 1. Introduction

Calcined clays can significantly modify the early hydration behaviour of cement. Especially the altered shape and position of the aluminate peak in calorimetry curves of calcined clay blended cement have attracted attention in recent studies. This has a practical background, as it is the reason for the increased sulfate demand in many blended cements. A correlation of C-S-H precipitated until the point of aluminate peak onset revealed two major sulfate hosts controlling the appearance of sulfate depletion peak: ettringite and C-S-H [1]. The presented paper therefore compares results from C<sub>3</sub>A model systems, where no C-S-H is present, with investigations in LC<sup>3</sup>-type systems, both incorporating different calcined clays and limestone. By using this approach, the mechanisms behind the increased sulfate demand of calcined clay blended cements can be further clarified and differentiated.

## 2. Methodology

The C<sub>3</sub>A reference system is made up of 10 wt% cubic C<sub>3</sub>A, 5 wt% sulfate carrier consisting of bassanite and gypsum (C $\bar{S}$ ), 85 wt% quartz powder (QP) and an alkaline model solution (MOH) with no portlandite. The QP was stepwise replaced with a calcined illitic clay (Cl) and a coarse (CKc) and fine (CKf) kaolinitic clay, while the C $\bar{S}$  was adjusted stepwise up to 20 wt%. The LC<sup>3</sup>-type system was created by using a Portland limestone cement (PLC) with an initial limestone content of 14.7 wt% that was blended with 30 wt% of four calcined clays with different metakaolin content that is indicated by the number (CC23, CC41, CC69, CC82) and one microlimestone ( $\mu$ LS). The early hydration of the systems was followed by isothermal calorimetry.

## 3. Results and discussion

The occurrence of the aluminate peak generally correlates well with the SSA of the systems at identical sulfate content (Figure 1). This correlation was explained by an accelerated C-S-H formation, triggered by the filler effect, leading to more sulfate adsorbed onto C-S-H before the aluminate peak [2]. This can be taken as an explanation for why the aluminate peak is also accelerated in the system PLC\_ $\mu$ LS, even though, there is no additional aluminum source. However, there are still significant differences between the system with limestone and those with calcined clays. Despite a stronger acceleration of the silicate reaction by the  $\mu$ LS compared to the calcined clays with higher SSA, the aluminate reaction appears at a later point. This indicates, that in the systems with calcined clays, there might be a further mechanism accelerating the aluminate reaction. This is confirmed by the results retrieved in the C<sub>3</sub>A model systems (Figure 1a). The correlation between SSA and appearance of the aluminate peak also exists in absence of C-S-H formation, indicating a further host for sulfate in calcined clay blended systems. The acceleration is only slightly lower in the systems with the illitic clay, which proves that the alumina content is not a dominant factor at this stage. Much more likely is an adsorption of sulfate – probably in combination with Ca<sup>2+</sup> - onto the negative surface area of calcined clay minerals. This could also explain the difference between the calcined illitic and kaolinitic clays, since calcined kaolinite is known to have a stronger negative surface charge than calcined illite under alkaline conditions [3]. This can also be taken as an explanation of the stronger acceleration of the aluminate reaction in cements blended with calcined clays. Other than the acceleration through sulfate adsorption onto C-S-H, which only forms steadily, the commonly large surface area of calcined clays is available at the very beginning of C<sub>3</sub>A hydration. In the calcined clay blended PLC, the position of the aluminate peak can be readjusted by an addition of sulfate carrier: Even though the aluminate peak appears at a similar

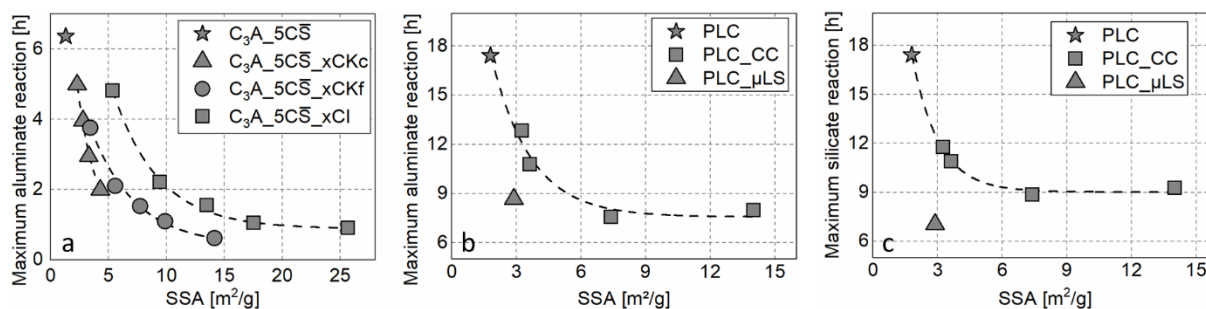


Figure 1 Correlation of the SSA of the systems with the occurrence of aluminate and silicate peak maximum. The surface area was varied using different replacement levels (a) or calcined clays with different SSA at the same replacement level (b, c). The maximum of the silicate reaction was retrieved from adequately sulfated systems. The aluminate maximum was determined in systems without sulfate adjustment.

point in time in the undersulfated PLC\_CC82 and PLC\_μLS, the latter system requires less sulfate to achieve a separation of the silicate and aluminate peak (Figure 2a,b). Another hint for a different mechanism in the calcined clay blended cement is the relationship between full width at half maximum (FWHM) and the position of the aluminate peak. It is well known that the latter becomes broader with higher amounts of sulfate added, however, here it is shown that the peak shape in the PLC\_CC systems is noticeably sharper compared to the PLC\_μLS systems, even when they occur at the same time (Figure 2c). This phenomenon, which indicates a faster ettringite precipitation, might as well be connected to the type of sulfate host before aluminate onset.

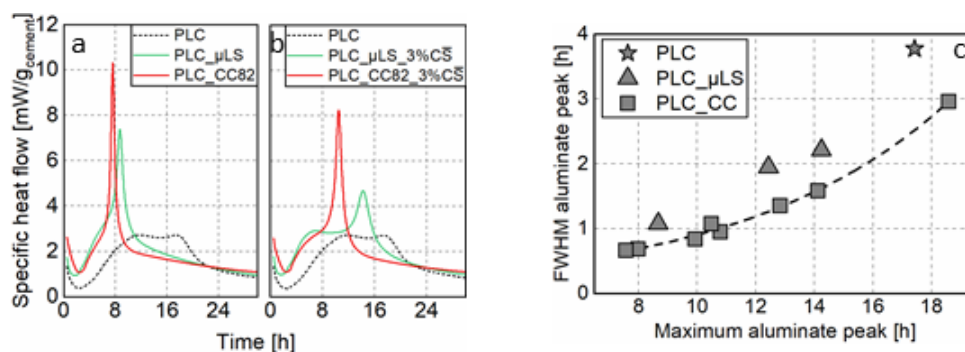


Figure 2 Heat flow of the PLC alone and blended with μLS and CC82 without sulfate adjustment (a) and with adjustment to 3 wt% C<sub>5</sub> (b). (c) shows the correlation between the peak maximum of the aluminate peak with its FWHM.

#### 4. Conclusion

The study reveals that there are significant differences between the acceleration mechanisms of the clinker hydration by calcined clays and classical fillers such as limestone. This can most likely be drawn back to sulfate adsorption onto calcined clay mineral surfaces. Cement blended with calcined clays of high purity therefore require notable more sulfate than cement blended with fillers or low-grade clays.

**Keywords:** C<sub>3</sub>A, aluminate reaction, early hydration, sulfate demand

#### 5. References

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